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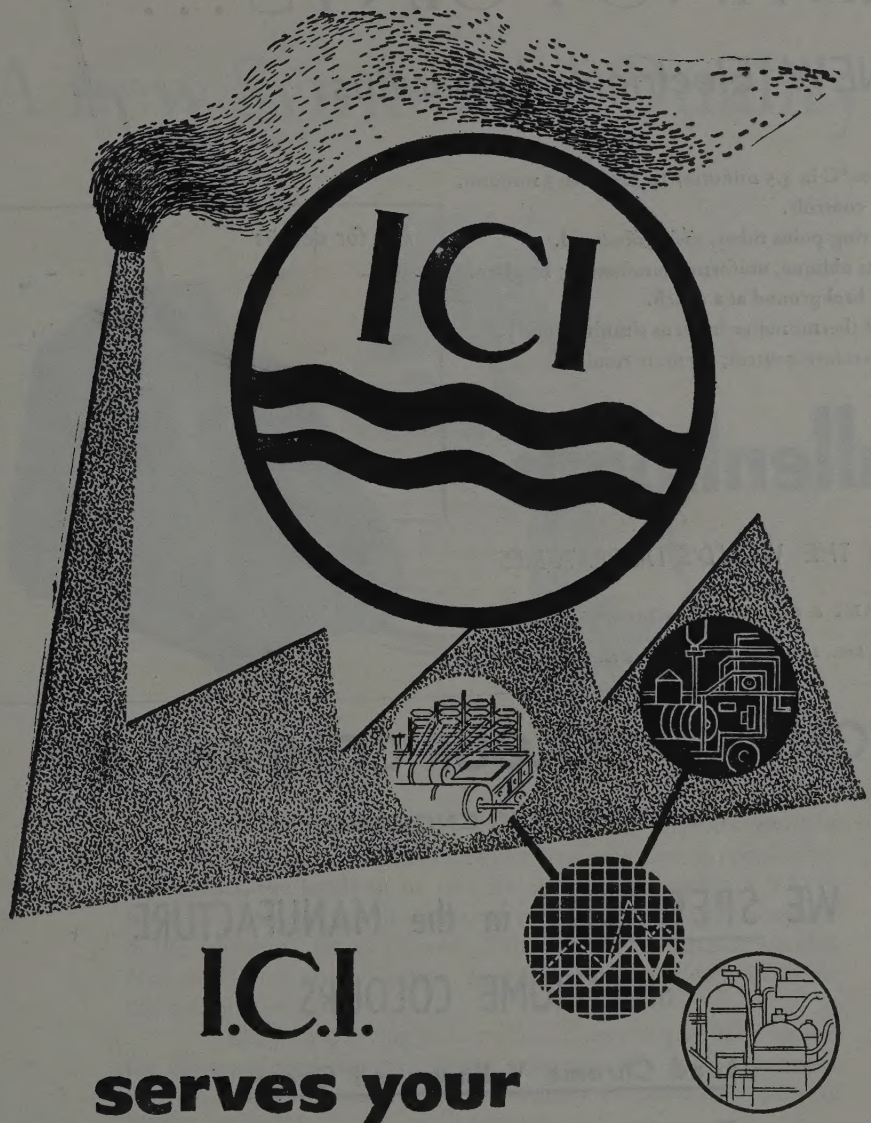

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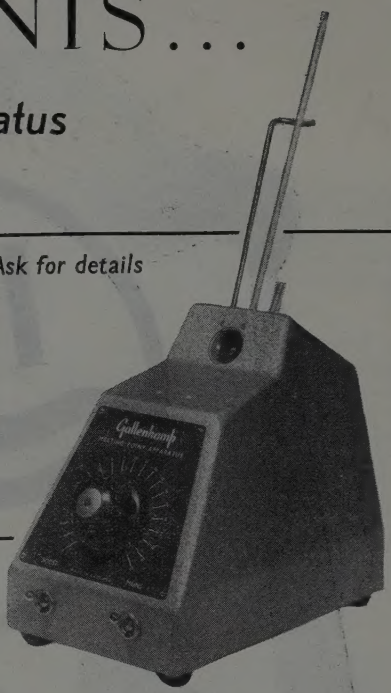

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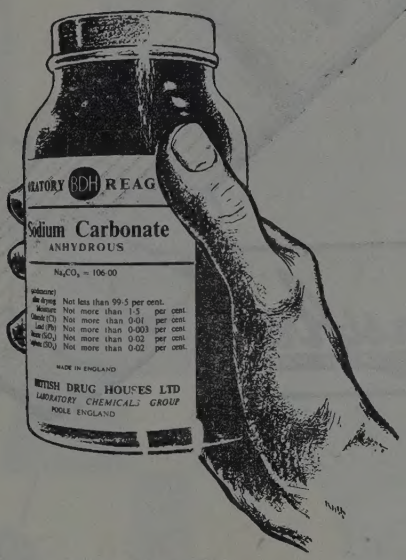

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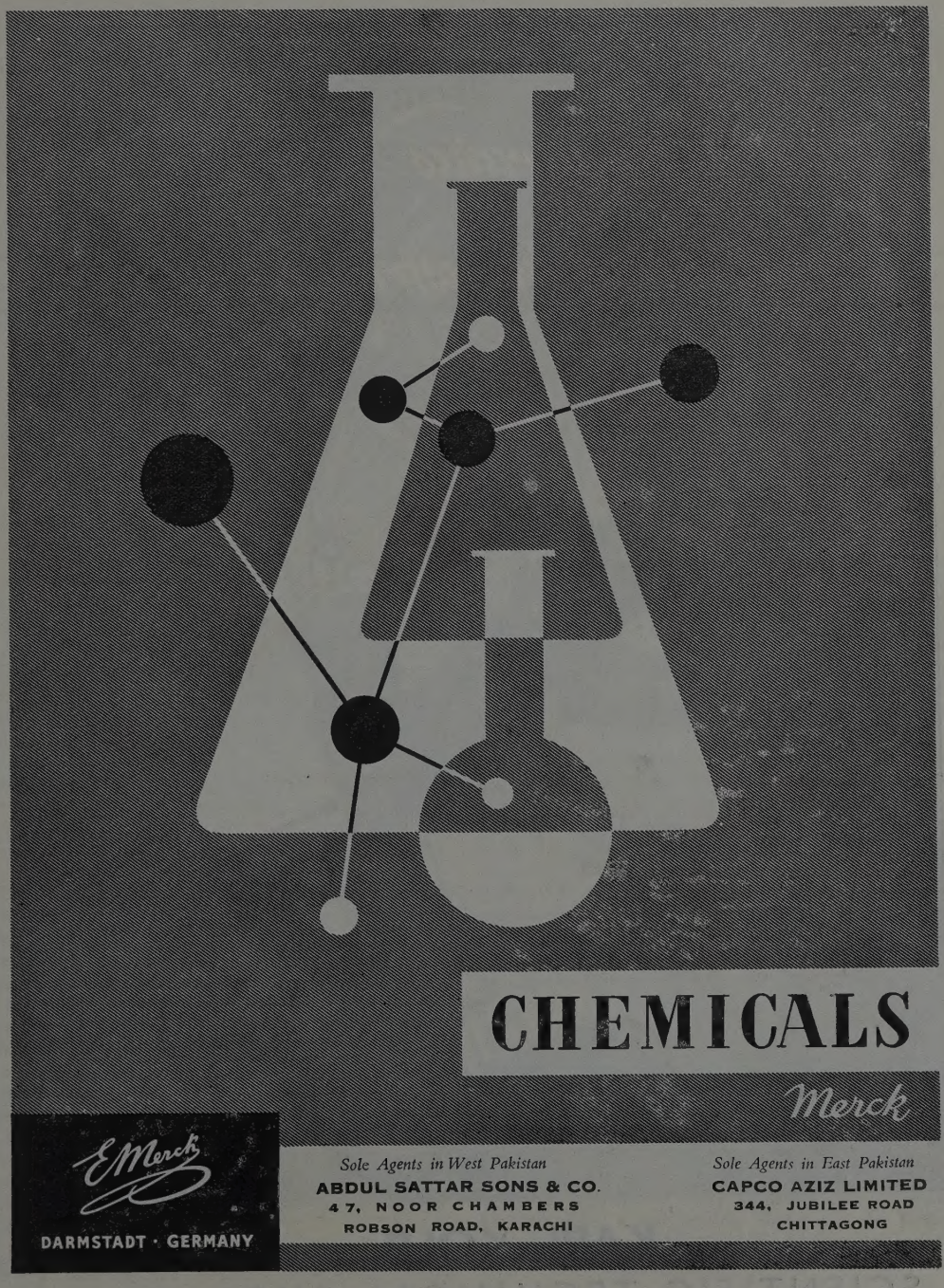
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QUANTITATIVE AND STRUCTURAL ANALYSIS OF KALABAGH IRON ORE BY PHYSICO-CHEMICAL METHODS WITH REFERENCE TO ITS BENEFICIATION

Part I.—Calibration of X-ray Spectrometer for the Estimation of Iron

Sadrul Hasan Rizvi and Mazhar Mahmood Qurashi

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1. Introduction

As the iron ore from Kalabagh (West Pakistan) has been generally recognized to be the most practicable source of iron for the steel industry of the country, it was considered of importance to undertake detailed analytical and structural studies on this ore by a combination of chemical and physical techniques, with a view to determining the optimum conditions for its beneficiation. Among the physical techniques, X-ray methods have been extensively employed, because of the ease and reliability they offer in providing information on the structural characteristics of minerals.

The use of X-rays in the investigation of minerals can be divided into three distinct categories, namely (i) quantitative estimation of different elements in the sample, (ii) identification of the various constituent crystalline phases in the sample, and (iii) detailed examination of the structural relationships of these various phases. Studies in all these respects, have been carried out on the Kalabagh ore, and the results will be presented in a series of communications on the subject. The X-ray fluorescence spectrometer has been extensively used during these investigations and the present paper describes the standardization of this instrument for an accurate estimation of iron in the raw ore and in the beneficiated samples.

X-ray spectroscopy utilises the characteristic secondary X-radiation from the elements in the test samples for their identification and quantitative estimation. The secondary X-rays, the K and L series lines of which are principally useful, are selectively reflected by a crystal grating which, when set in a position satisfying the Bragg relation, $\sin\theta = n\lambda/2d$, reflects the radiation of wave length λ on to the other side, where it can be picked up and its intensity measured by a Geiger counter (inset to Fig. 1(a)). Thus the glancing angle θ for the crystal setting identifies the radiation completely, and this in turn identifies the element producing it, while the intensity of this characteristic radiation is a measure of the quantity of the element present. Such a technique can therefore be used with advantage for both qualitative and quantitative analyses, especially for mineralogical and ore samples.

2. Basic Desiderata for the Analytical Work

The absolute value of intensity of a given reflection depends on various factors, such as, the intensity of the primary radiation, the thickness of the sample, its surface area exposed to X-rays, the particle size, and the composition of the matrix of the sample. The first four conditions can be standardised in a particular set-up but allowance for the composition of the matrix of samples presents a very considerable problem. In principle, a calibration curve can be drawn with standard samples containing known quantities of the test element and having essentially the

same matrix as the test material, and this curve can then be used for the analysis of the test samples. But in practice, this method is not suited for ore samples because of their complex and variable matrix, and for such cases the use of internal standards has been suggested.[1] The internal standard element has to satisfy two essential conditions : (1) that its emission line (the one that has to be used as its reference line) be close to the emission line of the test element, so that the disturbing effects due to the matrix of the sample will be identical for both the lines, and (ii) that the absorption edges of the standard and the test elements do not interact seriously with either of the reference lines. After the internal standard element has been selected, a calibration curve can be prepared with standard samples containing known percentages of the test element and the standard element. This calibration curve can then be used for the analysis of the test element in unknown samples.

3. Experimental Details

Equipment : A "Seifert" fluorescence spectrometer was used for this study, and a copper tube was used as the source of primary X-rays because it gives a higher sensitivity than other available tubes (Fig. 1). The surface area of the samples exposed to X-rays was maintained constant by keeping the relative position of the sample holder and the X-ray tube fixed. A lithium fluoride crystal, with planes of d-value equal to 2.00865 A.U. in the reflecting position, was used for analysing the characteristic secondary X-radiation given out by the elements in the sample. The spectrometer provided for scanning and automatic recording of the entire excited X-ray spectrum of the test sample, and also for the direct reading of the intensity of the lines in counts per second. The sensitivity of the Geiger counter could be varied with the help of the sensitivity selector switch to cover a full scale deflection of 10-30,000 c.p.s.

Sample Preparation : The sample was used in the powdered form, ground so that nearly all of it passed through a 100 B.S. sieve. Because the specimen had to be mounted vertically in the spectrometer used, it was first made into a paste with the help of a dilute amyl acetate solution of household cement, a commercial material used for joining plastic materials. This paste was then spread to a depth of approximately one millimetre on a glass slide about one inch square, thus providing enough material to receive the full spread of the incident beam. The slide dried fully in half an hour or so, and was then mounted in place on the spectrometer.

4. Semi-quantitative Calibration Curve for Elements Heavier than Titanium

An approximate calibration curve was initially prepared to obtain a rough measure of the sensitivity of the instrument for the different elements of the periodic table, the sensitivity being expressed as counts per second for one per cent element by

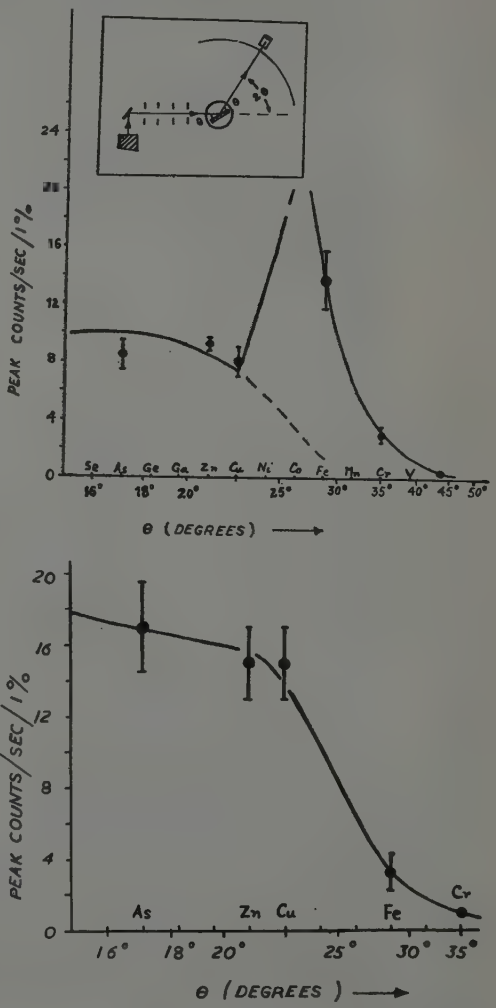

Fig. 1.—Semi-quantitative calibration curves from titanium to selenium with (a) copper tube (top) and (b) molybdenum tube, (bottom) both run at 45 kV and 20 mA. The short vertical lines indicate the variation of the experimental points with the matrix of the mixture, and the inset shows a schematic diagram of the spectrometer.

weight in a mixture composed of several compounds. A portion of this curve, covering the elements from titanium (atomic number 22) to selenium (atomic number 34) is shown in Fig. 1(a) and 1(b), that in Fig. 1(a) being obtained with a copper tube as the primary source of X-rays, whereas Fig. 1(b) shows the curve obtained with a molybdenum tube, both the tubes being run at 45 kV and 20 mA. These curves were obtained with standard calibrating samples prepared by mixing several compounds containing known quantities of test elements, different samples being prepared separately for the different parts of the periodic table, and the results finally checked by using a composite sample containing about fifteen elements spread over the full range, from $Z=20$ to $Z=92$. As expected, a considerable variation was found in the number of counts per second (for one per cent element by weight) when the composition of the matrix was changed, but the mean values plotted in Fig.1 may be taken to be correct to within their standard deviations, which are shown by the short vertical lines in the figure. These curves can, therefore, be used for a preliminary semi-quantitative estimate of the constituent elements of a mineral sample. This analysis is then used to define the optimum experimental conditions to be used for an accurate quantitative measurement, as described below for the Kalabagh iron ore samples.

It should be mentioned that in the present study the peak heights from the recorded traces of the various characteristic X-ray lines have been used. This procedure is justifiable provided that the operating conditions are kept constant, particularly with regard to scanning speed and time-constant of the rate-meter smoothing circuit. For the work described herein a scanning speed of 1° per minute was used, the capacitor of the smoothing circuit being kept fixed at a moderate value.

5. Quantitative Calibration Curve for Iron by the Method of Dilution-cum-Internal Standard

It can be seen from Fig. 1 that the sensitivity obtained with the copper tube in this range of the periodic table is higher than with the molybdenum tube, the copper tube giving almost three times as many counts as the molybdenum tube for the same percentage of iron content in any sample. This made the copper tube the preferred choice as the source of primary X-rays for the present work.

From the semi-quantitative analysis, it was known that the mean iron content of the ore sample was around 35%, and because the individual samples were expected to vary widely in iron content, therefore the calibration curve had to be drawn so as to cover a wide range, say from 15 to 60% iron. This meant (cf. the semi-quantitative calibration curve) that the peak heights of the Fe $K\alpha$ line would lie between 200 c.p.s. and 750 c.p.s. if the samples were used as such. Although the instrument counter is able to record such large counts accurately, yet the requirement that the calibration curve be prepared with standard calibrating samples having the same matrix as the test samples is impossible to meet, especially in view of the wide variations in the nature of the ore samples, which were from different areas and depths within the ore field. A partial solution of this difficulty is to dilute the test samples (by a large factor) with a suitable compound, and then to compare them with standard calibrating samples containing different quantities of the test element distributed in the same diluting agent. This method has its justification, because in this case the matrix of the test samples and the standard samples is essentially that of the diluting agent. The otherwise reliable method of incorporating a suitable element as an internal standard in the test samples and also in the calibrating standard samples for comparison, cannot by itself cope with the errors caused by a variable matrix.

Keeping in view the influence of a diluting agent in reducing the uncertain disturbing effects of the matrix, a method based on the combination of the dilution and the internal standard technique was developed for the present work. Calcium carbonate was used as the diluting agent and the dilution factor has been taken as ten. This dilution by a factor of ten will evidently reduce the intensity of the Fe $K\alpha$ line for the poorest standard calibrating sample to a low value of nearly 20 c.p.s., but this is no disadvantage since it can be accurately recorded by the counter. On the other hand, it will reduce the error caused by the presence of the variable matrix to a negligible value of less than 1%.* Cobalt was chosen as the internal standard element, because it is close enough to iron and its absorption and emission lines do not interact seriously either with the iron or the copper lines (from the exciting tube), as can be seen from the wavelengths given in Table 1.

Having thus made a choice of the diluting agent and the internal standard element, a standard "calibrating mixture" was prepared by

* This estimate is based on a dilution factor of 10 coupled with the variations in counting rate due to matrix variations seen in Fig. 1.

TABLE 1.—K-SERIES EMISSION LINES AND ABSORPTION EDGES OF IRON, COBALT AND COPPER

Elements	$K\alpha_2$ in A.U.	$K\alpha_1$ in A.U.	$K\beta_1$ in A.U.	K-absorption edge in A.U.
Iron	1.9399	1.9359	1.7565	1.7433
Cobalt	1.7927	1.7889	1.6207	1.6081
Copper	1.5443	1.5405	1.3921	1.3804

mixing cobalt in the form of cobalt acetate in calcium carbonate, so as to have nearly a 10% content of cobalt acetate in the mixture. The calibrating samples were then prepared by taking a constant quantity (about 4.5 g.) of the standard calibrating mixture and mixing it with known quantities of ferric oxide (Fe_2O_3) so as to obtain concentrations of 0.16% to 6% iron in the total mixture. Because a small mechanical mixer was not available, the mixing of each sample was done manually for fifteen minutes, the technique used being to add the "calibrating mixture" in three or four successive instalments with thorough mixing for five minutes between additions. A specimen record of counting rate against the angle 2θ is shown in Fig. 2. The experimental values of peak counts have been determined from the mean of two observations on the peak heights of the Fe Kα and Co Kα lines from two successive records for each standard sample. A calibration curve with log [H (FeKα)/ H (CoKα)] against log [C (Fe)/C (calibrating mixture)] was drawn as in Fig. 3, where H denotes peak heights in counts per second, and C denotes percentage concentration by weight in mixture. A fairly good straight line plot results, but the points for low percentages of iron tend to be rather widely scattered. This was suspected to be due to incomplete mixing of the samples, because the standard samples for obtaining these points had been prepared in a single step by mixing only a few milligrams of ferric oxide in about 4.5 grams of calibrating mixture. In order to improve the accuracy in this region, fresh standard samples were prepared starting from a single standard calibrating sample containing 8.6% Fe_2O_3, the weaker calibrating samples being made from this sample by successive dilution with the calibrating mixture. The results are given in Table 2. This technique gives better dispersal of the iron oxide, and a better calibration curve is obtained as shown in Fig. 4, thus confirming the importance of careful mixing. The previous calibration curve is also drawn in Fig. 4 (broken line) and is seen to be exactly parallel to the new curve for iron contents greater than 8%, which proves the accuracy of both sets of readings in this range.

6. Application and Discussion of the Calibration Curve

The deviations of the individual readings from the mean value are indicated by the circles around the points shown in Fig. 4, and a smooth curve has been drawn through them. It may be

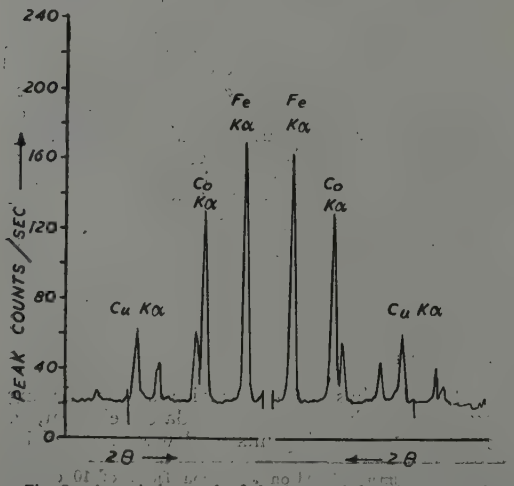

Fig. 2.—A typical record of the iron, cobalt and copper peaks obtained in two successive runs with a calibrating sample for iron estimation.

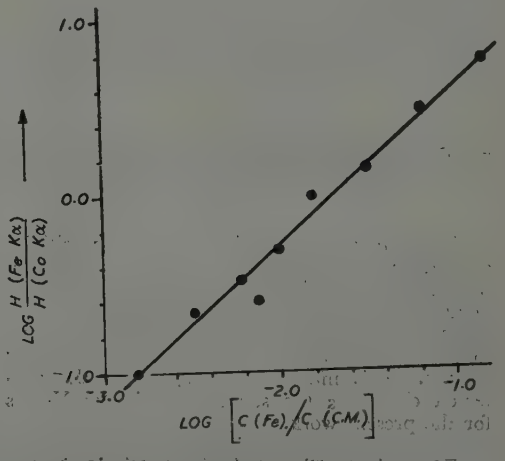

Fig. 3.—Logarithmic quantitative calibration curve for iron, showing large errors at small iron content due to imperfect mixing.

noted that this curve does not deviate far from a straight line. A number of analyses have been based on this curve and have given results in good agreement with the chemical analyses, the error being nearly ±1%. The outstanding advantages of this analytical technique are its simplicity and rapidity, which were of great value in following the course of ore beneficiation produced by various methods.

An attempt was also made to use the Cu Kα line from the X-ray tube itself as an internal

TABLE 2.—CALIBRATION DATA FOR PLOTTING THE CURVES IN FIGS. 4 AND 5.

Sl. No.	Percentage of iron in the total mixture	Percentage of the calibration mixture in the total mixture	$\log \frac{\%\ Fe\ in\ mixture}{\%\ calib.\ mixt.\ in\ the\ mixture}$	log % Fe in the mixture	Peak counting rate in counts/second			$\log \frac{H(FeK\alpha)}{H(CoK\alpha)}$	$\log \frac{H(FeK\alpha)}{H(CuK\alpha)}$
					Cu Kα	Co Kα	Fe Kα		
1	6.00	90.0	$\bar{2}.824$	0.778	48.5	166	336	0.306	0.841
2	3.17	94.7	$\bar{2}.525$	0.501	39.2	106	142	0.127	0.559
3	1.71	97.2	$\bar{2}.245$	0.233	48.0	149	92.5	$\bar{1}.793$	0.285
4	0.938	98.4	$\bar{3}.979$	$\bar{1}.972$	37.8	118	42.6	$\bar{1}.558$	0.052
5	0.517	99.1	$\bar{3}.717$	$\bar{1}.714$	48.0	136	35.3	$\bar{1}.415$	$\bar{1}.867$
6	0.287	99.5	$\bar{3}.460$	$\bar{1}.458$	38.3	106	20.4	$\bar{1}.284$	$\bar{1}.726$
7	0.159	99.7	$\bar{3}.203$	$\bar{1}.202$	54.3	161	16.2	$\bar{1}.003$	$\bar{1}.475$

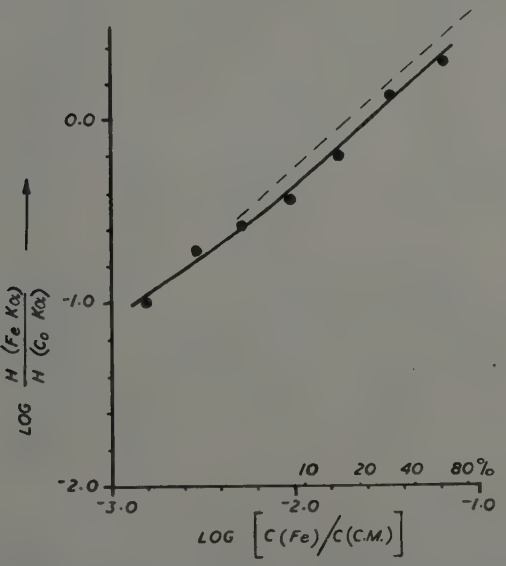

Fig. 4.—Logarithmic calibration curve for iron obtained from samples with improved mixing. The broken line corresponds to the curve of Fig. 3, and the per cent figures given along the abscissa denote the corresponding iron content for an unknown sample on the basis of 10% dilution.

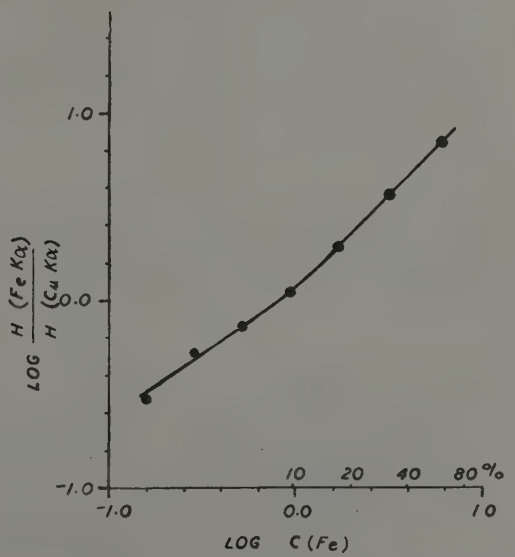

Fig. 5.—Logarithmic calibration curve obtained using the copper Kα line from the tube as an internal standard. The per cent figures along the abscissa denote the corresponding iron content of an unknown sample on the basis of 10% dilution.

standard, first because the ore sample itself does not contain copper and secondly because the Cu $K\alpha$ line is also close to the Fe $K\alpha$ line. A calibration curve with log [H (Fe $K\alpha$)/ H(Cu $K\alpha$)] against log C(Fe) was drawn, and is given in Fig. 5. The deviations of individual points from the mean value have been estimated, as before, from measurements on two successive records, and are of the order of the radii of the circles shown in the figure. Although this calibration curve appears to be somewhat better than that shown in Fig. 4, the nature of the two curves is essentially the same. This indicates that the characteristic radiation of the tube itself can be very profitably used as an internal standard, provided, of course, that the test sample does not contain the target element in appreciable quantities. This method would have the added advantage that an external element does not need to be introduced into the sample, and thus the uncertainties pertaining to its improper mixing are eliminated.

It must, however, be noted that the success of any method of calibration for analytical work will eventually be determined by the nature of the ore sample, and individual cases have to be studied on their own merits before choosing the most suitable method.

Acknowledgement

The authors are indebted to Mr. Abdul Hai and Mr. Ainul Hasan Khan for kindly supplying the analysed ferric oxide standard, and to Mr. Latif Ahmad and Mr. Mohammad Sualehin for their help with some of the experiments.

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CHEMICAL EXAMINATION OF LORANTHUS GREWINKII BOISS AND BUNGE

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Loranthus grewinkii is a fruit tree parasite found in West Pakistan and in many parts of Iran, especially in the northern provinces of Gilan and Mazandran, on pear, apricot and almond trees. Morphologically it is similar to *Viscum album*, but differs from it in the colour of the fruits and the size of the leaves.[1]

The plant is locally known as "Keshmesh kowli" "Mavize Kohi" and also "Mavizaj-e-kohi". The dried berries which carry only one seed, are dark brown in colour, have a shrivelled surface and contain a sticky material which can be drawn out in threads. It is highly valued in the Unani system of medicine as a general nerve tonic, and is also reputed for its properties as a resolvant and a laxative,[2] but no chemical investigation of its constituents appears to have been carried out. The present studies have been carried out with the locally available, stored material. On extraction with light petroleum (b.p. 60-80°C.) a sticky resinous material was obtained (yield about 35%), which on hydrolysis with alcoholic potash gave about half of its weight as unsaponifiable matter (15% on the weight of the berries). From the unsaponifiable matter two triterpenoids have been obtained through their benzoyl derivatives, one of which has been identified as lupeol ($C_{30}H_{50}O$) while the other, which analyses for the formula, $C_{30}H_{50}O_2$, (m.p. 224-26°(sub.) $[\alpha]_D^{20} = +4.5$ ($CHCl_3$) appears to be new and has been provisionally named as "loranthol" (yield 5.9% on the weight of the unsaponifiable fraction).

Loranthol gives crystalline diacetyl and dibenzoyl derivatives and would thus correspond to a dihydroxy compound, belonging most probably to the same series of triterpenoids as lupeol. This view finds a measure of support from the infrared studies, which confirm the presence of two hydroxyl groups in loranthol as against one in lupeol and also point to their structural similarity (Figs. 1 & 2).

The two products were separated from each other on the basis of the varying solubilities of their benzoyl derivatives in hot light petroleum (b.p. 60-80°C.). Loranthol dibenzoate is almost insoluble in this solvent, while lupeol benzoate readily goes into solution in hot petroleum ether. The presence of lupeol was established by physical and chemical means through comparison with an authentic sample prepared from the unsaponifiable fraction of *Holarrhena antidysenterica*.[3]

Further work on the mother liquor of the two benzoates and other constituents of the berries is in progress.

Experimental

500 g. of the berries were first soxhleted with petroleum ether (b.p. 60-80°C.) and the exhausted material was then crushed and extracted by soxhleting with ethyl alcohol. The latter extractive was freed of the solvent and digested with petroleum ether, and the combined ethereal extracts were freed of the solvent, yielding 175 g. of a brownish sticky mass (35%). This product was saponified with 7% alcoholic potassium hydroxide and worked up in the usual manner, when it yielded 75 g. of unsaponifiable matter (yield 15% on the weight of the berries). The unsaponifiable matter which gave a strong sterolic colour reaction (Liebermann-Burchard) resisted crystallization through the usual solvents.

Benzoylation of Unsaponifiable Matter: Lupeol and Loranthol Benzoates.— 45 g. of the unsaponifiable material was refluxed in benzene solution (50 cc.) with benzoyl chloride (20 cc.) and pyridine (15 cc.) for 10 hours on a water bath. Water was then added to the reaction mixture and the whole was extracted out with 1:1 mixture of benzene and petroleum ether. The extract was repeatedly washed with water, dried over anhydrous sodium sulphate, concentrated to a small volume under reduced pressure, and kept in the cold when it yielded 9.4 g. of a colourless crystallisate, the mother liquors failing to yield any further crystalline matter.

The crystallisate was extracted out with hot petroleum ether. The petroleum ether soluble portion gave on repeated crystallisation from this medium a product which finally melted at 265°C. (yield 5.5 g.) and gave on hydrolysis a product melting at 210-12°C. which analysed for lupeol, $C_{30}H_{50}O$, and gave no depression in melting point on admixture with an authentic sample of lupeol.

Calculated for $C_{30}H_{50}O$: C, 84.5 ; H, 11.7 ; O, 3.8 ; m.w., 426. Found : C, 84.76 ; H, 11.74 ; O, 3.88 ; m.w., 441.

The benzoate which analysed for $C_{37}H_{54}O_2$ also showed no depression in mixed melting point with a sample of lupeol benzoate.

Calculated for $C_{37}H_{54}O_2$: C, 83.7 ; H, 10.1 ; O, 6.04 ; m.w. 530. Found : C, 83.1 ; H, 10.11 ; O, 6.4 ; m.w., 464.

The petroleum ether insoluble fraction of the initial crystallisate was repeatedly crystallised through a mixture of chloroform and acetone till a product finally melting at 340°C. (dec.) was obtained (stout rods, yield 8.7%). This product which is nearly insoluble in petroleum ether, ether and alcohol, sparingly soluble in ethyl acetate readily so in benzene and chloroform, analysed for $C_{44}H_{58}O_4$.

Calculated for $C_{44}H_{58}O_4$: C, 81.19 ; H, 8.98 ; O, 9.83 ; m.w. 650. Found : C, 80.7 ; H, 8.93 ; O, 9.62 ; m.w., 573.

Loranthol.—0.147 g. of the dibenzoate as obtained above was refluxed with 10 cc. of 10% alcoholic

Fig. 3.—Tetrahedral loranthol crystals from acetone solution (x 5 nearly).

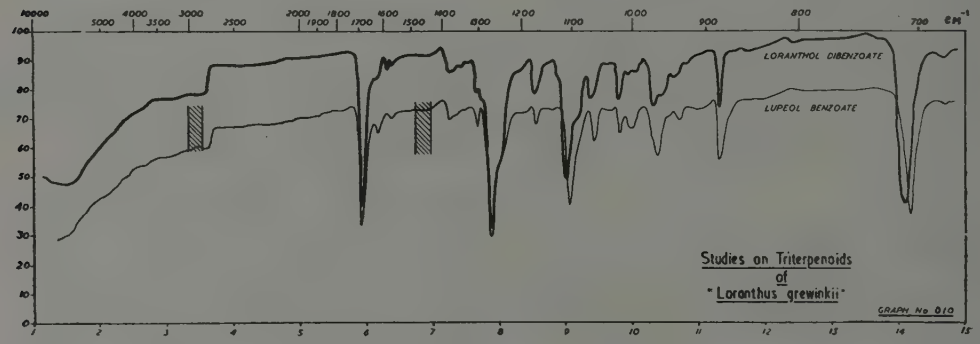

Fig. 1.—Infra-red spectra of lupeol benzoate and loranthol dibenzonate (oil "mulls", concentration 2/3 mg./cm.²)

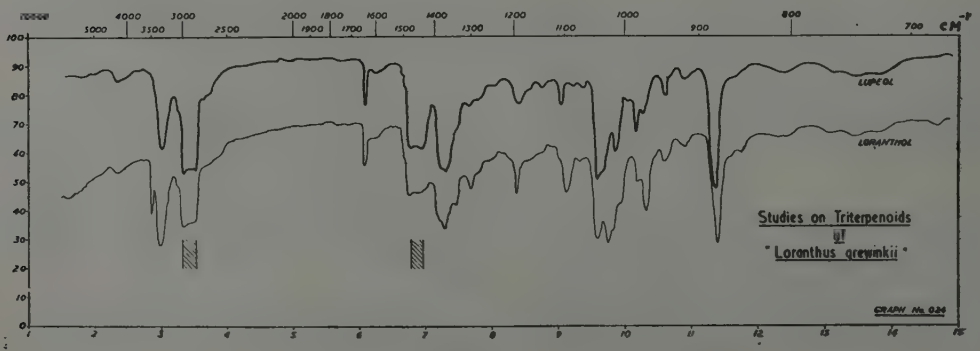

Fig. 2.—Infra-red spectra of lupeol and loranthol (oil "mulls", concentration 2/3 mg./cm.²)

Potassium hydroxide till the solution became clear. The reaction mixture was nearly freed of the solvent *in vacuo* and after addition of water repeatedly extracted with benzene. The benzene extract was thoroughly washed with water, dried over anhydrous sodium sulphate, filtered and freed of the solvent *in vacuo*. On crystallisation of the oily residue from a mixture of ether and petroleum ether by slow evaporation at room temperature loranthol was obtained in nearly theoretical yield ; m.p. 224-26 °C. (with partial sublimation). On recrystallisation from acetone it gave tetrahedral type of crystals (Fig. 3). Loranthol is easily soluble in ether, ethyl acetate, alcohol, chloroform and benzene, sparingly soluble in hot petroleum ether and acetone. Loranthol analysed for $C_{30}H_{50}O_2$.

Calculated for $C_{30}H_{50}O_2$: C, 81.39 ; H, 11.38 ; O, 7.23 ; m.w., 442. Found : C, 81.35 ; H, 11.49 ; O, 7.5 ; m.w., 418.

Loranthol Diacetate.—0.12 g. of loranthol was refluxed with 10 cc. of acetic anhydride for 6 hrs. with the addition of a drop of concentrated sulphuric acid. The reaction mixture was then poured over crushed ice and extracted with ethyl acetate. The ethyl acetate solution was repeatedly washed with sodium bicarbonate (10%) and then with water, dried over anhydrous sodium sulphate and freed of the solvent. On repeated crystallization of the glassy residue from methanol, loranthol diacetate was obtained as longish rectangular plates which melted at 220-21 °C. and analysed for $C_{34}H_{54}O_2$.

Calculated for $C_{34}H_{54}O_2$: C, 77.52 ; H, 10.3 ; O, 12.15. Found : C, 77.70 ; H, 9.8 ; O, 12.25

Infra-red Studies.—The infra-red curves of lupeol benzoate and loranthol dibenzoate (Fig. 1) indicate a general similarity albeit with small but definite variations especially in the 900 cm.$^{-1}$ to 1200 cm.$^{-1}$ region. Further the graph for loranthol (Fig. 2) shows two separate peaks in the hydroxyl region (3500 cm.$^{-1}$), as against the single peak in case of lupeol. This difference is confirmed by definite differences in the 1000 cm.$^{-1}$ to 1.100 cm.$^{-1}$ region, which is also sensitive to the hydroxyl groups.

The spectra were obtained on a Leitz double beam spectrometer equipped with a sodium chloride prism. All spectra were determined on oil suspensions or mulls of powdered substances, the concentration of the substance in the beam being nearly 2/3 mg./cm.^{2}

Acknowledgement

The authors are indebted to Dr. M.M. Qurashi for carrying out the infra-red studies of these compounds and contributing to their interpretation. We are also indebted to Mr. Attaullah Khan for helping with the experimental work.

Grateful acknowledgement is made for the help kindly given by Dr. G. Taylor, Director, Royal Botanic Gardens, Kew, Richmond, Surrey, England ; Dr. M. Zahir, Director General, Ministry of Agriculture, Iran; and Dr. Abdul Hafiz, Director, Food and Agriculture Council, Government of Pakistan, in connection with the identity of the drug.

Microanalyses were carried out by A. Bernhardt, Max Plank Institut, fur kohlenforschung, 22 a Mülheim (Ruhr), W. Germany.

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PAPER CHROMATOGRAPHY OF THE ALKALOIDS OF RAUWOLFIA SERPENTINA

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Introduction

The isolation of the alkaloidal complex, serpajmaline,[1] from the fresh undried roots of *Rauwolfia serpentina* has given a fresh impetus to studies in this field in consequence of the fact that this complex, which mainly contains the stronger bases, serpentine, serpentinine, ajmaline and two unknown substances, and is chromatographically free from reserpine, has a strong hypotensive action without any sedative central-depressant action responsible for the undesirable side-effects of reserpine in the treatment of hypertension.[2] Serpajmaline is obtained in the form of a light cream coloured powder, readily soluble in water. In the course of its isolation, a number of other water-insoluble complexes, mainly consisting of the weaker bases, were obtained. For facilitating studies in the composition of these complexes in respect of their individual basic constituents, a need was felt for evolving a suitable technique for their paper chromatographic analysis, which would give a clear picture of the alkaloidal constituents.

While studying the antifertility effects of reserpine and the metabolism of the *Rauwolfia* alkaloids in man and in laboratory animals, Boscott and Kar[3] made use of a number of solvent systems for the separation of these alkaloids by paper chromatography. They have also mentioned some tests for locating these compounds on the paper, but no reference has been made to either the fluorescence or the shape of the spots thus located. Even the R_F values recorded for the following two solvent systems showed overlapping of spots, thus restricting their application to pure samples of the alkaloids, rather than to their mixtures. Their solvent systems were (1) 1% acetic acid in aqueous 5% sodium acetate shaken with *n*-butyl ether, added in small quantities until saturation : the clear aqueous phase was used. (2) Similar to (1) but using tertiary amyl alcohol instead of *n*-butyl ether.

Starting out from the results obtained by these authors, the present investigation was carried out to examine more closely the usability of some of their single phase solvent systems and to devise a solvent which could give a wider range of R_F values and hence a better separation of individual bases in the alkaloidal mixtures.

Method

The following authentic samples of the alkaloids of *Rauwolfia serpentina*, were used in the present investigation : 1. Rescinnamine. 2. Reserpine. 3. Reserpinine. 4. Serpentine. 5. Serpentinine. 6. Ajmalicine. 7. Ajmaline.

The ascending chromatographic technique of Axelrod and Bandurski[4] was employed. A suitable quantity of the alkaloid in chloroform was applied to one corner of Whatman paper No. 1, about 3 cms. from the bottom and side edge. The size of the paper depends upon the dimensions of the bell jar, and 20 × 25 cms. was found suitable in our case. The paper was formed into a cylinder and stapled together with fine threads,

Table 1.—Comparative Efficiencies (in Terms of R_F Values) of Whatman Paper Nos. 1 and 542.

Solvent : Aqueous layer obtained by saturating 10% acetic acid (v/v) in 5% sodium acetate with *n*-butyl ether.

Type of paper	Rescinnamine	Reserpine	Reserpinine	Serpentine	Serpentinine	Ajmalicine	Ajmaline
Whatman No. 542 ..	0.26	0.34	—	0.50	—	—	0.76
Whatman No. 1 ..	0.29	0.39	0.54	0.50	0.37	0.57	0.78

avoiding contact of the adjacent edges, and then suspended by a hook inside the bell jar, placed on a well-greased glass sheet supporting a petri dish containing the solvent. By lowering the hook, the paper was dipped in the solvent system, and the chromatogram was allowed to run until the solvent almost reached the upper edge of the paper, about five hours being required for this purpose. The paper was then thoroughly dried in the air at room temperature and viewed under ultra-violet light.

Experimental

Preliminary experiments were conducted to ascertain the efficiency of Whatman paper No. 1. Using the same solvent system, the R_F values on No. 1 were compared with those obtained by Boscott and Kar on Whatman paper No. 542. From Table I, it seems reasonable to conclude that the two papers are at par with each other.

The location of *Rauwolfia* alkaloids on the paper presented considerable difficulties. It has been reported that when the alcoholic layer, obtained by shaking butanol, hydrochloric acid and water, was taken as the developing solvent, ajmaline took two weeks to become visible under ultra-violet light.[5] In the course of efforts for devising tests to locate the *Rauwolfia* alkaloids on paper, it was observed that ajmaline could be readily detected in ultra-violet light after the paper has been sprayed with a 5% solution of sodium acetate.* Table 2 hows the data obtained on the shape and fluoresence of the spots for the *Rauwolfia* alkaloids.

TABLE 2.—THE SHAPE AND FLUORESCENCE OF RAUWOLFIA ALKALOIDS SEPARATED ON WHATMAN PAPER NO. 1.

Alkaloids	Shape of spots after development	Fluorescence
Rescinnamine ..	Streak	Light green
Reserpine ..	Elongated	Light green
Reserpinine ..	Oval	Bright green
Serpentine ..	Oval	Sky blue
Serpentinine ..	Streak	Violet
Ajmalicine ..	Oval	Light blue
Ajmaline ..	Round	Violet changing to light blue.

After a few trials it was observed that the addition of methanol to the above mentioned solvent system showed a marked effect on the R_F values of all the standard alkaloids. This addition gave a solvent system that could give a clean separation of the alkaloidal mixtures as shown by Table 3. The addition of methanol, in some way, also affects the rate of capillary ascent, thereby reducing the time of the development of the chromatogram. The solvent was prepared in the following manner :—

Acetic acid 1% (v/v) in aqueous 5% sodium acetate is shaken with isobutyl methyl ketone,

* Since the solvent suggested by Boscott and Kar incorporated sodium acetate buffer, the difficulty of locating ajamaline was not encountered by them.

TABLE 3.—THE R_F VALUES, SHAPE AND FLUORESCENCE OF THE RAUWOLFIA ALKALOIDS AFTER DEVELOPMENT WITH THE NEW SOLVENT.

Alkaloids	R_F Values	Shape	Fluorescence
Rescinnamine ..	0.12	Oval	Light green
Reserpine ..	0.22	Oval	Light green
Reserpinine ..	0.40	Round	Bright green
Serpentine ..	0.33	Round	Sky blue
Serpentinine† ..	—	Elongated	Violet blue
Ajmalicine ..	0.49	Round	Light blue
Ajmaline ..	0.74	Round	Violet changing to Light blue.

†R_F Value omitted due to the elongated nature of the spot.

added in small quantities until saturation. To 100 cc. of the clear aqueous phase is added 5 cc. methanol, which is then used for development. A typical composite chromatogram made in this way is shown in Fig. 1, and the measured R_F values together with other data are given in Table 3.

Fig.—A composite chromatogram (6/13 size) showing separation of Rauwolfia alkaloids.

Discussion

The addition of methanol to the solvent seems to affect the movement of all the bases in such a way that a wider range of R_F values is obtained, and the spots become round and compact. This has resulted in a better and clearer separation of the alkaloidal mixtures.

The fluorescence behaviour of ajmaline is somewhat peculiar. It was noted that the authentic samples of ajmaline gave a violet fluorescence which finally changed to light blue, the change being very gradual, so that more than 12 hours are required for the attainment of the final light blue colour. In natural extracts of *Rauwolfia serpentina*, *e.g.*, serpajmaline, on the other hand, ajmaline always gave the typical light blue fluorescence, no violet tinge being noticed. Further work relating to studies in this interesting behaviour of ajmaline is in hand.

Acknowledgement

The author wishes to express his indebtedness to Dr. Salimuzzaman Siddiqui for suggesting the problem. His sincere thanks are also due to Dr. Rolf Deininger for his very keen interest and valuable suggestions throughout this work. For the supply of some of the authentic samples of alkaloids the author is indebted to Bochringer Mannhein.

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THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

Part II.—The Temperature Dependence of the Viscosity of Hydroxylic Compounds. Preliminary Activation Energy Data on Glycerol and Ethylene Glycol

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Introduction

In Part I of this paper, some results were presented on the temperature variation of the viscosity of certain mineral oils over a range extending from 5°C. to 130°C.[1] In the final analysis, the measured viscosity was fitted to an Andrade-type equation,

$$\ln \eta = \ln A + \frac{\varepsilon}{kT}, \qquad (1)$$

with variable ε and A, ε being obtained from the derived relation

$$-T^2 \frac{d(\ln \eta)}{dT} = -\frac{T^2}{\eta}\frac{d\eta}{dT} = \frac{\varepsilon}{k} = \frac{E}{R}, \qquad (2)$$

where ε measures the mutual potential energy between neighbouring molecular aggregates, and E is the same energy per mole, R being the gas constant and k the Boltzmann constant. The curves for E/R (or ε/k) and lnA against the absolute temperature T showed evidence for the existence of certain definite states of the liquids in which ε and A are constant, the transition between these states being gradual and smooth, as shown schematically in Fig. 1. However, since the mineral oils used in these experiments

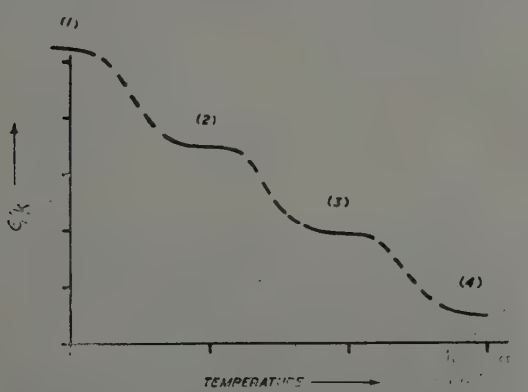

Fig. 1.—Schematic representation of segments in the curves of activation energy of viscous flow in mineral oils.

are known to be mixtures of several closely related hydrocarbons, the data obtained with them are not easy to interpret with certainty. In order to study the significance of this succession of definite states, and to correlate them with the behaviour of the molecular aggregates, it was therefore considered advantageous first to extend the observations to several pure liquids, especially those containing hydroxyl groups, capable of forming hydrogen bonds between adjacent molecules.

Ethylene glycol and glycerol are two readily available liquids of this type, glycol possessing two hydroxyls per molecule and glycerol three, thus providing considerable possibilities of a high degree of aggregation (chelation), especially at low temperatures not far above the melting points. The present communication deals with the preliminary results obtained with these two liquids, together with a discussion of the improvements in experimental technique that are necessary to obtain accurate measurements of the step-wise variation in the inter-aggregate potential energy.

Apparatus and Experimental Details

To obtain measurements of any worthwhile accuracy on the polyalcohols glycerol and ethylene glycol, two precautions must be taken : (a) the experimental liquid must be purified by repeatedly distilling and drying under reduced pressure, and (b) the entry of moisture from the atmosphere into the viscometer containing the liquid must be guarded against. The dryness of these liquids is particularly important, because their viscosity is extremely sensitive to dissolved water, *e.g.*, the presence of 0.1% water lowers the viscosity of glycerol by 2%, and of ethylene glycol by about ½%. In order to keep the liquids as dry as possible during the viscometric readings, drying tubes were attached to each limb of the U-tube viscometers, which were of the British Standard Specifications pattern. Furthermore, a half-litre bottle with a special three-way stop-cock was used as a ballast tank (Fig. 2) and trap to prevent any water-vapour entering the viscometer due to a sudden release of the suction when the liquid is being sucked up into the upper bulb of the viscometer. The three-way stop-cock serves to

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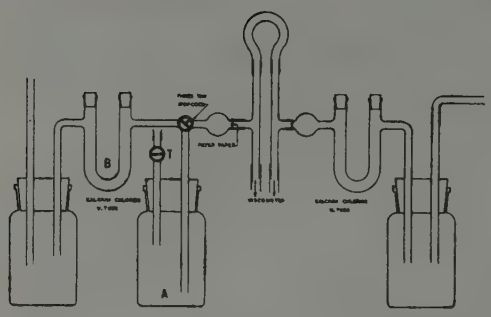

Fig. 2.—Sketch showing layout of water-vapour traps and ballast bottle for raising the liquid in the capillary limb of the viscometer

connect the left-hand limb of the viscometer either with (A) the half-litre bottle, or directly with (B) the drying tube. With the rubber tube connecting the two limbs of the viscometer pinched in the middle and the stop-cock in position 'A', a suitable quantity of air is sucked out of the bottle, after which the stop-cock T in the inlet to the bottle is closed. The liquid in the viscometer rises slowly in the left-hand limb, and when it is about 1 cm. above the upper mark, the three-way cock is turned to position 'B', thus isolating the ballast bottle and connecting the left-hand limb of the viscometer to the atmosphere through the drying tube. The pressure on the rubber connection at the top of the viscometer is also released, and the liquid flows down freely for the measurement of flow time. (The outer stop-cock T on the ballast bottle can be opened at leisure so as to bring the bottle to atmospheric pressure). With the above simple arrangement, it is possible to exercise very fine control over the rate of rise of liquid in the left-hand limb and at the same time to ensure that only dry air is introduced into the viscometer.

For measurements at high temperatures, the glycerol thermostatic bath designed for the work on lubricating oils, and described in Part I of this paper, is eminently suitable because it ensures temperature control to within one or two hundredths of a degree centigrade in the range of 70°C. to 250°C. For temperatures lower than 70°C., efficient stirring becomes difficult due to the high viscosity of the glycerol, and therefore a water-bath is preferable. The viscometer was supported vertically in the bath and a thermometer of appropriate range placed with its bulb close to the middle of the viscometer. Since the literature showed that previous experimental measurements of the viscosities of glycerol and ethylene glycol are limited to a few temperatures between 0°C. and 50°C., the first step was to make a general survey of the variation of viscosity of these two liquids from room temperature to as high a temperature as is practicable without excessive oxidation or loss of the test liquid by evaporation. For this purpose, it was considered sufficient to measure the kinematic viscosity of the liquids at intervals of 10°C., and to calculate the value of the quantity,

$$-\frac{T^2}{1000}\,\frac{\Delta \ln \nu}{\Delta T} = \frac{E'}{R}\Big/ 1000, \qquad (3)$$

in the middle of each ten-degree interval. E' differs from the energy E (cf. equation 2) by a small correction for the use of the kinematic viscosity ν, in place of the dynamic viscosity η. From the calculations given in Appendix I of Part I of this paper, it is clear that

$$\frac{E}{R} = \frac{E'}{R} + T^2 \times \beta, \qquad (4a)$$

where β is the coefficient of cubical expansion of the liquid at temperature T. Contrary to the usual practice of drawing graphs for $\ln \eta$ against $1/T$ and measuring their slope at various points, we have considered it better to calculate the activation energy, E, directly from successive observations. This method is preferable because it eliminates the uncertainties in drawing the tangent to a graph and enables a more reliable picture of the variation of E with temperature to be obtained.

Since an accuracy of about 2% in E was thought to be sufficient for the general survey, an ordinary thermometer graduated in degrees centigrade was used in conjunction with a magnifying thermometer-reader to obtain the temperature reading correct to 0.1° C. (After this preliminary survey had been made, it was found desirable to increase the accuracy of the measurements of E by a factor of two and also to decrease the interval between successive viscosity measurements to 5°C.; altogether this necessitates a four-fold increase in the accuracy of the temperature measurement).

The level of the liquid in the viscometer was adjusted after intervals of approximately 30°C., because the rise in level is only 2 to 3 mm. for every 10°C., and it is preferable to keep the liquid isolated under dry conditions as far as possible with a minimum of exposure to the ordinary atmosphere. The volume of liquid was adjusted so that at the beginning of this 30°-interval, the level was about 4 mm. *below* the mark, hence at the end of this interval it would be nearly the same height *above* the mark. The

correction for the variation of level with temperature and for the kinetic-energy term in the viscometer formula,

$$\nu = A\,t - \frac{B}{t},$$

was applied by means of the formula developed in Part I (Appendix I) of this paper, which is

$$-\frac{\Delta \ln \nu}{\Delta T} = -\frac{\ln (t_2/t_1)}{T_2 - T_1}\left(1 + 2\,\frac{B/A}{t^2}\right) + \frac{\alpha}{100}\,\frac{x_2 - x_1}{T_2 - T_1}, \qquad (4b)$$

where t_1 and t_2 refer to the times of flow at temperatures T_1 and T_2, and x_1, x_2 are the corresponding heights of the liquid level above the mark on the large bulb of the viscometer. The constant 'α' is the percentage increase in time of flow produced by 1 cm. rise of the level above the mark, and it is nearly equal to 1.0 for the viscometers used in our work.

Results with Glycerol

To begin with, the exploratory experiment was performed to determine the general variation of viscosity and of $\frac{E'}{R} = -T^2\,\frac{\Delta \ln \nu}{\Delta T}$ with temperature. For this purpose, redistilled glycerol was used and the times of flow in the appropriate viscometers were measured every 10°C. from room temperature (nearly 30°C.) upto 200°C. In this range of temperature, the viscosity fell from about 460 centistokes to 1.5 centistokes — a range of 1 : 300 — so that, the measurements had to be taken with two B.S.S. U-tube viscometers, namely Nos. 3 and 2. The data obtained are given in Table 1, and they show that $\frac{E'}{R}/1000$ drops monotonically from over 7 at room temperature to about 3 at 200°C.

This table shows that if we measure ΔT and $\Delta \ln \nu$ accurate to one percent, the error in $\frac{E'}{R}/1000$ will vary from about 0.10 at low temperatures to 0.04 at 200°C. However, it usually happens that the errors of measurement of both ΔT and $\Delta \ln \nu$ increase somewhat at higher temperatures, so that the error in $\frac{E'}{R}/1000$ in the exploratory experiment may be taken to be *nearly uniform* at a figure of about 0.1 or a little lower. This exploratory experiment also showed that, although the times of flow in viscometer No. 2 at the highest temperatures are much less than one minute (the minimum being 30 seconds), satisfactory accuracy can be obtained by using a stop-watch graduated in tenths of a second, thus permitting measurement to 0.02 second. In this way, the use of viscometers Nos. 1 and 0 with very fine capillaries, is avoided, thus reducing the chances of error due to small particles that may find their way accidentally into the experimental liquid.

For the more detailed measurements, redistilled glycerol was dried over sulphuric acid in a vacuum desiccator until bubbles ceased to rise from the glycerol. In this way, the water content of the glycerol can be kept well below 0.1%. Care was also taken when filling the viscometer to dry it by passing a stream of dry air through it. For each determination of viscosity, the bath was maintained at the desired temperature for fifteen to thirty minutes before the flow time was measured four to five times in succession. The temperature was also noted along with each measurement of the time of flow, and the mean values of both were used in the calculations. The observations were taken continuously between 25°C. and 210°C., using viscometer No. 3 from 25°C. to 75°C. and viscometer No. 2 from 70°C. upwards. In the lower temperature range, the viscometer was supported inside a standard electrically controlled water-bath with a temperature stability of 0.01°C., while for the higher temperature range the special glycerol thermostat was used. Table 2 gives the values of $(-10\,\Delta \ln \nu/\Delta T)$ calculated from the observed times of flow both with rising temperature sequence and falling temperature sequence. The agreement between the two sets of values is seen to be quite good, the standard deviation being about 1%. The individual deviations (from the mean) are given for values of $\frac{E'}{R}/1000$ calculated from the corresponding means for $-10\,\Delta \ln \nu/\Delta T$. The standard deviation for $\frac{E'}{R}/1000$ is seen to be 0.04 in each of the two ranges of the table. The results are plotted in the upper graph of Fig. 3(b) and show the presence of steps of the kind envisaged in the introduction (Fig. 1), especially at the higher temperatures.

The corresponding plot of $\ln \nu$ against $1/T$ in Fig. 3(a) gives some idea of the improved discrimination obtained by calculating the values of E'/R from successive observations instead of trying to split up the curve for $\ln \nu$ against $1/T$ into a series of linear segments. (It is worth noting here that Benedick (private communication to Prof. Antonoff) has advocated the use of the first derivative, $d\phi/dT$ to bring out the discontinuities

Table 1.—Exploratory Experiment with Redistilled Glycerol.

Temp. (°C.)	35	45	55	65	75	85	95	105	115	125	135	145
$-10\Delta\ln\nu/\Delta T$	0.744	0.657	0.572	0.506	0.441	0.398	0.338	0.318	0.285	0.252	0.223	0.200
$\frac{E'}{R}/1000$	7.08	6.63	6.17	5.78	5.34	5.10	4.58	4.55	4.30	4.00	3.71	3.50

Temp. (°C.)	150	160	170	180	190
$-10\Delta\ln\nu/\Delta T$	0.193	0.187	0.170	0.147	0.142
$\frac{E'}{R}/1000$	3.46	3.51	3.34	3.02	3.04

Table 2.—Approximate Data for Glycerol from 30°C. to 205°C.

Mean temp. in °C.	$-10\Delta\ln\nu/\Delta T$ Rising	Falling	Mean	$\frac{E'}{R}/1000 = -\frac{T^2}{1000}\frac{\Delta\ln\nu}{\Delta T}$	Mean temp. in °C.	$-10\Delta\ln\nu/\Delta T$ Rising	Falling	Mean	$\frac{E'}{R}/1000 = -\frac{T^2}{1000}\frac{\Delta\ln\nu}{\Delta T}$
30	0.794	0.786	0.790	$7.26_4 \pm .04$	130	0.236	0.240	0.238	$3.88_4 \pm .02$
35	0.741	0.732	0.7365	$6.99_1 \pm .04$	135	0.235	0.227	0.231	$3.85_1 \pm .08$
40	0.689	0.692	0.6905	$6.78_2 \pm .01$	140	0.218	0.218	0.218	$3.72_4 \pm .01$
45	0.651	0.659	0.655	$6.62_4 \pm .04$	145	0.205	0.213	0.209	$3.66_4 \pm .07$
50	0.615	0.605	0.610	$6.37_4 \pm .06$	150	0.196	0.200	0.198	$3.55_4 \pm .03$
55	0.563	0.563	0.563	$6.08_4 \pm .00$	155	0.196	0.198	0.197	$3.61_4 \pm .01$
60	0.544	0.546	0.545	$6.05_4 \pm .01$	160	0.189	0.187	0.188	$3.53_4 \pm .01$
65	0.516	0.512	0.514	$5.88_4 \pm .03$	165	0.174	0.170	0.172	$3.31_4 \pm .04$
70	0.472	0.466	0.469	$5.52_4 \pm .04$	170	0.170	0.172	0.171	$3.36_4 \pm .01$
75	0.453	0.466	0.4595	$5.56_4 \pm .07$	175	0.168	0.172	0.170	$3.42_4 \pm .03$
80	0.428	0.428	0.428	$5.33_4 \pm .00$	180	0.154	0.156	0.155	$3.18_4 \pm .02$
85	0.404	0.393	0.3985	$5.11_4 \pm .07$	185	0.156	0.150	0.153	$3.22_4 \pm .07$
90	0.378	0.386	0.382	$5.04_4 \pm .05$	190	0.148	0.148	0.148	$3.18_4 \pm .00$
95	0.354	0.358	0.356	$4.82_4 \pm .03$	195	0.125	0.131	0.128	$2.81_4 \pm .07$
100	0.331	0.324	0.3275	$4.56_4 \pm .05$	200	0.128	0.124	0.126	$2.82_4 \pm .05$
105	0.305	0.299	0.302	$4.32_4 \pm .04$	205	0.124	0.123	0.123_5	$2.82_4 \pm .01$
110	0.288	0.292	0.290	$4.25_4 \pm .02$					
115	0.275	0.281	0.278	$4.19_4 \pm .05$					
120	0.272	0.264	0.268	$4.14_4 \pm .06$					
125	0.248	0.248	0.248	$3.93_4 \pm .00$					
				Std. deviation $= .04_2$					Std. deviation $= .04_1$

in a measured property, ϕ. Our technique of calculating $-T^2 \frac{d \ln \nu}{dT} = -\frac{T^2}{\nu}\frac{d\nu}{dT}$ is better still because (a) it directly measures the energy, and (b) this function varies very slowly with the temperature, T, while the values of $d\nu/dT$ are approximately proportional to ν, and therefore vary rapidly with temperature, thus making the identification and interpretation of the segments in the curve rather difficult. Even the function, $\frac{d \ln \nu}{dT} = \frac{1}{\nu}\frac{d\nu}{dT}$, is open to this objection, though in lesser degree). The magnitude of the difference in $\frac{E'}{R}/1000$ between successive steps in Fig. 3(b) lies between 0.15 and 0.3, which is 3 to 7 times the standard deviation of the individual points, and should therefore be significant. This, however, presupposes that other disturbances, such as thermometer error, are negligibly small. To check this point, and at the same time to obtain another set of observations of E′/R, a part of the experiment was repeated with another thermometer, also graduated to 1 °C., and therefore capable of being read to 0.1 °C. The points obtained with this second thermometer in the range 75 °C. to 150 °C. are plotted in the lower graph of Fig. 3(b), which is labelled "Thermometer II" and is displaced downwards by 0.5 unit. The means of the two sets of observations are plotted in the upper curve of Fig. 4, the short vertical lines in which are equal to the estimated standard deviation. It is seen that, although the graphs obtained with two different thermometers show a number of similar variations, nevertheless

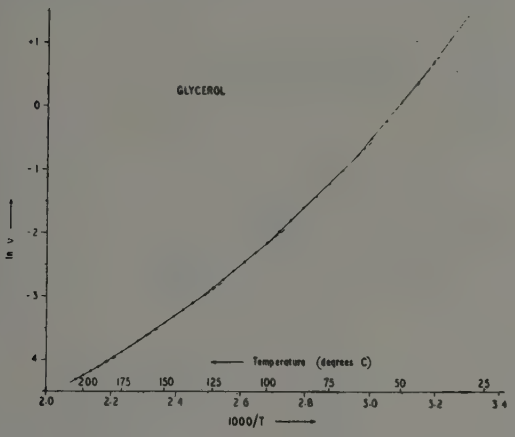

Fig. 3.—(a) Graph for ln ν against 1000/T for glycerol between 25 °C. and 205 °C., showing linear segments.

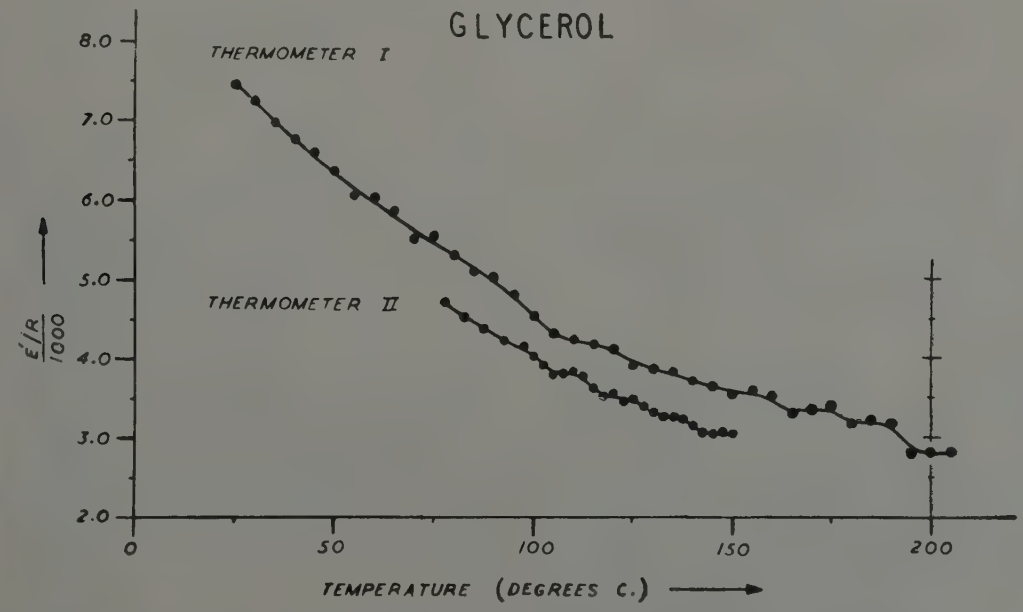

Fig. 3 (b).—Alternative graphs of activation energy, $\frac{E'/R}{1000}$, against temperature for glycerol, showing the presence of steps. The radius of the solid circles corresponds to the standard error.

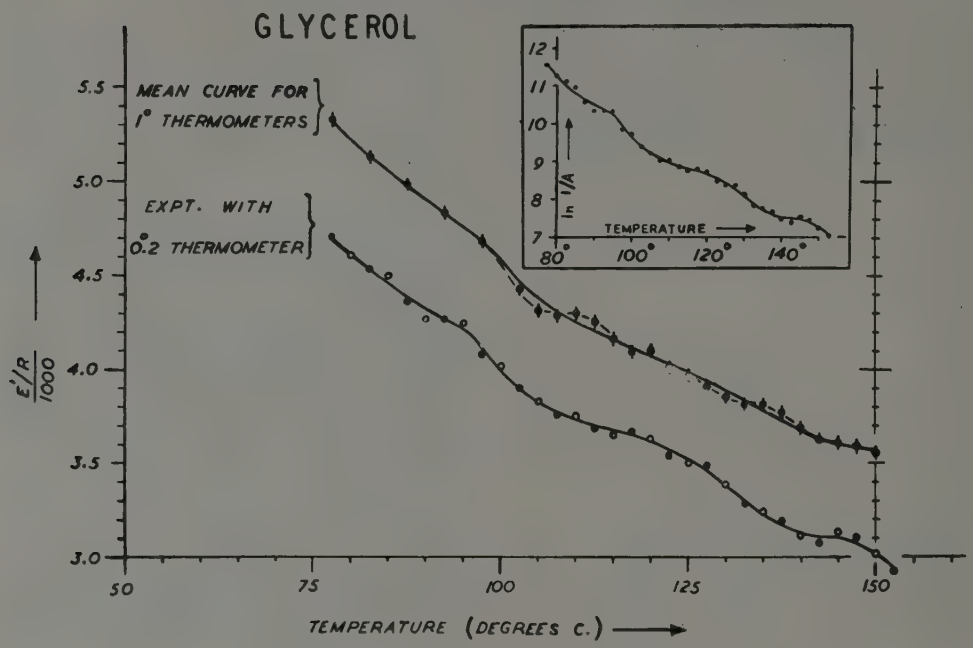

Fig. 4.—Accurate graphs of $\frac{E'/R}{1000}$ and ln (1/A) for glycerol from 75°C. to 155°C., showing the presence of segments with an interval of 25°C. The standard errors of the points are indicated by the short vertical lines and the radii of the circles in the three graphs.

the differences between the two are also considerable. The solid line in the mean graph of Fig. 4 shows the most probable form of the curve, and indicates segmentation at intervals of about 25°C. The broken line which passes through almost all the points includes the contribution of the thermometric errors. However, it is possible that some of the variation indicated by this broken line may be genuinely due to the experimental liquid.

It is therefore necessary to increase considerably the accuracy of the temperature measurement, which is the chief source of inaccuracy in the above observations. Only then can the experimental values of E′/R be relied upon to give a correct picture of the segments or steps observed in the graphs. Accordingly, two good-quality thermometers graduated to 0.2° C. in the ranges 45°C. to 105°C. and 95°C. to 155°C. were selected. (They were compared at various temperatures with two other thermometers of the corresponding ranges and the differences were found to be of the order of 0.01° to 0.03° C., indicating that the individual thermometers could be relied upon to somewhat better than this). The complete set of observations between 75°C. and 150°C. was retaken in the high temperature thermostat with these thermometers, according to the plan of Table 2, but with the interval $\Delta T = 5$°C. between successive readings. Table 3 shows this set of observations together with another such set taken at the intermediate temperatures, so that we now have an experimental value of $\frac{E'}{R}$/1000 at every 2.5° C. These values are all plotted in Fig. 4, being displaced downwards through 0.5 unit below the mean curve for the two previous experiments made with coarser thermometers. The solid circles correspond to the first set of observations in Table 3, and the hollow circles to the second set. The standard deviation of the individual points of the new graph is seen from Table 3 to be only 0.020, *i.e.*, one-half of the figure for the previous graphs, inspite of the fact that the interval, ΔT, has been reduced by a factor of two.

The new graph confirms the conclusions derived from the previous mean graph, and shows very clearly that the complete curve for E′/R against

TABLE 3.—MORE ACCURATE DATA FOR GLYCEROL FROM 75°C TO 150°C.

Mean temp. in°C.	$-10\frac{\Delta \ln \nu}{\Delta T}$ (deviations are given x10⁴)	$\frac{E'}{R}/1000 = -\frac{T^2}{1000}\frac{\Delta \ln \nu}{\Delta T}$	Correction $= \frac{T^2\beta}{1000}$	$\ln \frac{1}{A}$ (corrected)	Mean temp. in°C.	$-10\frac{\Delta \ln \nu}{\Delta T}$ (deviations are given x10⁴)	$\frac{E'}{R}/1000 = -\frac{T^2}{1000}\frac{\Delta \ln \nu}{\Delta T}$	Correction $= \frac{T^2\beta}{1000}$	$\ln \frac{1}{A}$ (corrected)
77.5	0.4226±13	5.21±0.02		11.55	75.0			0.067	
82.5	0.3980± 8	5.04±0.01		11.12	80.0	0.4088±20	5.11±0.03		11.28
87.5	0.3731± 8	4.86±0.01	0.074	10.58	85.0	0.3887±17	5.00±0.02		10.97
92.5	0.3560± 9	4.77±0.01		10.36	90.0	0.3605± 6	4.76±0.01		10.34
97.5	0.3322± 7	4.58±0.01		9.85	95.0	0.3499± 8	4.75±0.01		10.32
102.5	0.3110±11	4.40±0.02		9.38	100.0	0.3244± 4	4.52±0.01	0.082	9.73
107.5	0.2935±13	4.26±0.02		9.02	105.0	0.3030± 3	4.33±0.00		9.23
112.5	0.2814± 6	4.19±0.01	0.090	8.86	110.0	0.2893± 7	4.25±0.01		9.01
117.5	0.2725± 5	4.17±0.01		8.80	115.0	0.2756± 9	4.15±0.01		8.77
122.5	0.2577± 9	4.04±0.01		8.48	120.0	0.2669±12	4.13±0.02		8.71
127.5	0.2481±11	3.99±0.02		8.37	125.0	0.2517±10	4.00±0.02	0.099	8.36
132.5	0.2292± 7	3.78±0.01		7.84	130.0	0.2390±11	3.89±0.02		8.12
137.5	0.2188± 8	3.69±0.01	0.118	7.66	135.0	0.2243±13	3.74±0.02		7.76
142.5	0.2066± 6	3.57±0.01		7.38	140.0	0.2117± 3	3.61±0.01		7.46
147.5	0.2033±11	3.60±0.02		7.44	145.0	0.2074±10	3.63±0.02		7.51
152.5	0.1883±15	3.42±0.03		7.03	150.0	0.1957±14	3.51±0.02	0.137	7.23
		Std. deviation=0.020					Std. deviation=0.020		

temperature consists of a series of segments of the type sketched in Fig. 1, each segment covering a range of about 25°C. in temperature and 0.25 in $\frac{E'}{R}/1000$. The various segments are apparently identical in shape, starting with a steep drop and ending with a practically horizontal portion as the temperature is raised. The degree of agreement between the two graphs of Fig. 4 is such as to confirm that the precision of the more accurate experiments (cf. Table 3) is enough to bring out correctly the general shape of these segments, while the previous experimental data contain a large proportion of random error, comparable with the magnitude of the effects being investigated.*

Finally, with the data of Table 3, we can calculate the values of ln 1/A using equation (1), thus

$$\ln \frac{1}{A} = \frac{\epsilon}{KT} - \ln \eta = \frac{E/R}{T} - \ln \eta \qquad (5)$$

E/R is obtained from Table 3, while the corresponding values of ln η are readily derived from the observed times of flow. The results of the calculation are set out in columns 5 and 10 of Table 3, and are presented graphically in the inset of Fig. 4. ln 1/A decreases monotonically with rise of temperature, and the graph is seen to have nearly the same shape as that for the energy, E; this is due to the dominance of the first term on the right hand side of equation (5). The value of ln 1/A decreases by about 1.4 in going from one segment to the next, so that A increases by a factor of exp. (1.4) = 4. Bearing in mind that A is directly dependent on the concentration of the molecular aggregates in the liquid, this four-fold increase is suggestive of a corresponding diminution in size of the aggregates after each step of

*There is however some indication in the points that the lower graph of Fig. 4 may actually involve some small variations with a smaller temperature interval than 25°C., but the decision for this must await still more accurate measurements.

25 °C. However, further investigation is necessary before such an interpretation can be fully developed.

Results with Ethylene Glycol

The curves of Fig. 4 provided sufficient encouragement for taking up the study of ethylene glycol, which has two hydroxyl groups instead of the three in glycerol. Although glycol has a much lower viscosity than glycerol, it can be expected to show effects similar to glycerol, possibly with somewhat different characteristics. One thing is certain, namely, that accurate measurements of $\Delta \ln \nu/\Delta T$ will be more difficult, because, for a given ΔT, the quantity $\Delta \ln \nu$ is smaller for less viscous liquids, cf. the values of $(-10\ \Delta \ln \nu/\Delta T)$ at higher temperatures in Tables 2 and 3. To attain this accuracy, it was found expedient to take the observations every 5 °C., as for glycerol, but to use a larger interval for ΔT, *viz.*, 10 °C., for calculating $\Delta \ln \nu/\Delta T$. In this way the requisite accuracy can be obtained, although with the sacrifice of some of the detail in the variation of the energy E.

Since the viscosity of ethylene glycol is only a fraction of that of glycerol, viscometers must be used having finer capillaries than before. U-tube viscometer No. 2 was used from room temperature upto 90 °C., at which temperature the time of flow fell to about three quarters of a minute, and U-tube viscometer No. 1 was used for the higher temperatures upto 160 °C. Accurate measurements at temperatures higher than this were not feasible with our simple experimental arrangement because of errors introduced by excessive evaporation of glycol (boiling point = 198 °C.). Distilled glycol was dried thoroughly over sulphuric acid in a vacuum desiccator and then introduced into the viscometer with suitable precautions against the absorption of moisture. The times of flow were measured at intervals of 5 °C. as described in the previous section on glycerol, and the values of $(-10\Delta \ln \nu/\Delta T)$ and $\frac{E'}{1000R} = \frac{-T^2}{1000}\frac{\Delta \ln \nu}{\Delta T}$ were calculated with $\Delta T = 10$ °C. in order to obtain sufficient accuracy. The results are shown in Table 4, where the heading "Expt. I" refers to the first complete experiment performed with both rising and falling temperature sequences as in Tables 2 and 3. Due to the very small values of $\Delta \ln \nu$ at the higher temperatures, the precision at these temperatures was still poor (due probably to evaporation effects) and therefore another complete set of observations was taken from 85 °C. to 150 °C. The data obtained from this are shown under the column headed "Expt. II". By taking the mean values for the two experiments, an accuracy of about $\pm$ 0.025 was obtained in the measured value of $\frac{E'}{R}/1000$ over the entire range of temperatures.

The final results are shown graphically in Fig. 5, which again shows very clearly the presence of the step-like segments of Fig. 1. The different steps are nearly as definite as those in the final curve of Fig. 4 for glycerol, except at the lower temperatures, where there is some lack of clarity. The essential differences between the results for the two liquids are that (a) the temperature interval between successive "steps" is about 15 °C. for ethylene glycol as against 25 °C. for glycerol, and (b) there is a corresponding decrease in the magnitude of the jump in energy for each step. It is worthwhile to consider for comparison the available data for ethyl alcohol, which has only one hydroxyl group per molecule. The lower graph of Fig. 5 is drawn from calculations made with the standard data of Thorpe (1894), Titani (1927), and others.[2] It shows a clear division into segments with a repetition interval of about 30 °C., but, in contrast to the curves for glycerol and glycol, the "steps" are upwards instead of downwards. However from the general trend of the curve, it is reasonable to expect that at lower temperatures (*i.e.*, well below the boiling point) the graph for ethyl alcohol will become similar to those for glycol and glycerol. To check this point and to obtain more accurate data for the shape of the segments, it is proposed to study ethyl alcohol down to a few degrees above its freezing point.

Discussion and Lines for Further Work

The above observations suggest that the arrangement of the step-like segments is characteristic of the liquid being studied and that it will be very interesting to study the laws governing the interval between successive steps, both as regards the energy difference, ΔE, and the temperature difference. Such a study, if carried out for a number of related liquids, should give considerable insight into the mechanism responsible for the regular occurrence of these steps. It is worth noting here that Fig. 4 indicates that, at least for glycerol, the melting point (18 °C.) will lie on the steep part of one of the earlier segments of the graph for E against temperature. This is in agreement with similar measurements on supercooled liquids by Urazovski and Chernyavski, and suggests that the steep part of each segment corresponds to a structural transition. Since the interval, $\Delta E/1000R$, between successive segments is of the order of 0.15 for glycol and for

TABLE 4.—PRELIMINARY DATA FOR ETHYLENE GLYCOL FROM 30°C. TO 155°C.

Mean temp. in°C.	$-10\Delta \ln \nu/\Delta T$ Expt. I	Expt. II	Mean	$\frac{E'}{R}/1000 = -\frac{T^2}{1000}\frac{\Delta \ln \nu}{\Delta T}$	Mean temp. in °C.	$-10\Delta \ln \nu/\Delta T$ Expt. I	Expt. II	Mean	$\frac{E'}{R}/1000 = -\frac{T^2}{1000}\frac{\Delta \ln \nu}{\Delta T}$
30	0.388	—		3.56±.03	105	0.180	0.175	0.177_5	2.54±.02
35	0.367	—		3.49±.02	110	0.175	0.171	0.173	2.54±.02
40	0.344	—		3.37±.01	115	0.155	0.162	0.1585	2.39±.04
45	0.324_5	—		3.28±.01	120	0.146	0.157	0.1515	2.34±.06
50	0.308_5	—		3.22±.02	125	0.1495	0.1515	0.150_5	2.38±.01
55	0.291_5	—		3.14±.03	130	0.144_5	0.142_5	0.143_5	2.33±.01
60	0.277_5	—		3.07±.01	135	0.135	0.135	0.135	2.25±.00
65	0.285	—		2.95±.02	140	0.127_5	0.1325	0.130	2.22±.03
70	0.252	—		2.96±.02	145	0.129	0.130	0.129_5	2.26±.01
75	0.239_5	—		2.90±.03	150	0.130_5	0.124_5	0.127_5	2.27±.04
80	0.221	—		2.75±.03	155	0.123_5	0.121_5	0.122_5	2.24±01
85	0.219	0.212	0.2155	2.76±.03					
90	0.2085	0.2075	0.208	2.74±.01	Std. deviation of $\frac{E'}{R}/1000$ is :—				
95	0.197_5	0.198_5	0.198	2.68±.01					
100	0.186_5	0.184_5	0.185_5	2.58±.01	(a) 0.02_6 from 30° to 80°C. (b) 0.02_5 from 85°C. to 155°C.				

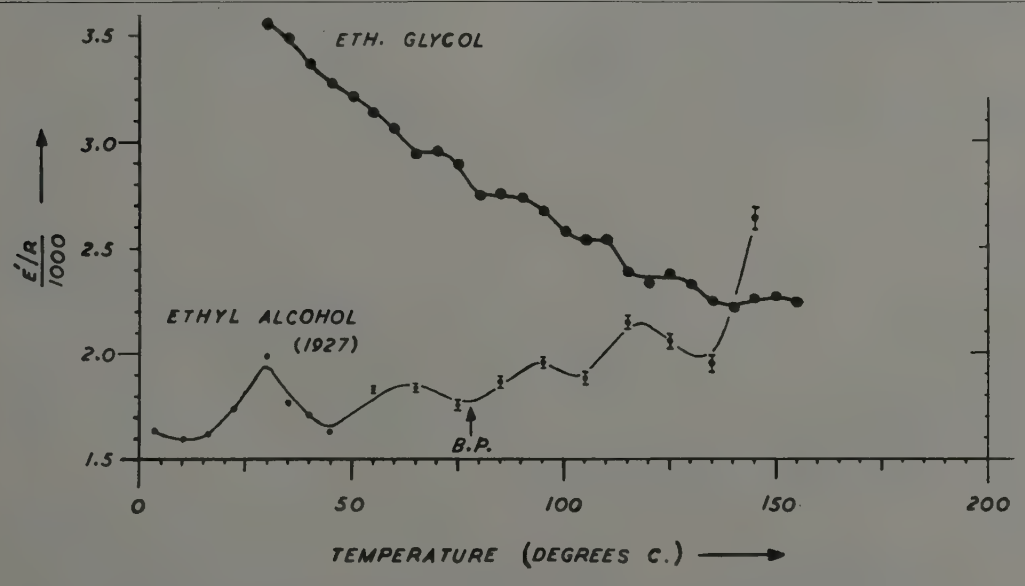

Fig. 5.—Graphs of $\frac{E'/R}{1000}$ for ethylene glycol and ethyl alcohol below 150°C. The radii of the solid circles and the short vertical lines indicate the estimated standard deviations of the points in the two graphs.

ethyl alcohol, and the present measurements have a standard error of 0.026, it is clearly necessary to increase the accuracy still further before the dependence of ΔE on temperature can be properly studied. Moreover, it will also be necessary to decrease the interval, ΔT, between successive viscosity measurements (5°C. for glycerol and 10°C. for glycol) to about 2°C. in order to obtain true representation of the variation of E from one step to the next. Such a decrease in the measuring interval, ΔT, necessitates a further corresponding increase in the accuracy of the measurements of both temperature and time of flow.

Thus, if we wish to attain an accuracy of 0.01 in $\frac{E}{R}/1000 \simeq \frac{T^2}{1000}\frac{\Delta \ln t}{\Delta T}$, which has a value of 4 ± 2, we must measure both $\Delta \ln t$ and ΔT to an accuracy of $1/2 \times 0.01/4$, *i.e.*, 0.12%, which requires an accuracy of better than 0.002 degrees centigrade in each temperature reading when the interval ΔT is taken as 2°C. This degree of accuracy is attainable either with a Beckmann differential thermometer or with a platinum resistance thermometer. Of these two, the Beckmann thermometer is somewhat easier to handle and has the further advantage of a smaller bulb and a quicker response to temperature changes.

There remains the matter of obtaining a corresponding accuracy in the measurement of $\Delta \ln t$, which can be accomplished if t_1/t_2 is measured to an accuracy of 1 part in 10,000. This requires a somewhat higher accuracy in the measurement of each individual time of flow, which is attainable provided certain precautions are taken. For instance, if the time of flow is 300 seconds and readings are taken to 0.01 second (by estimation), an accuracy of 1 part in 30,000 is possible. Further details of the measurements will be discussed in Part III of this paper, which deals with the accurate experiments on ethylene glycol and their interpretation.

It is hoped in subsequent communications to present also the results obtained from equally accurate experiments on ethyl alcohol, glycerol, methyl alcohol, water, and mixtures of these liquids in various proportions. The experiments on mixtures are expected to be especially illuminating because of the control that can be exercised through the concentration parameter. Later on, it will be feasible to include non-polar liquids also within the framework of the investigation.

Acknowledgement

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QUANTITATIVE AND STRUCTURAL ANALYSIS OF KALABAGH IRON ORE BY PHYSICO-CHEMICAL METHODS WITH REFERENCE TO ITS BENEFICIATION

Part II.—Analysis of Representative Samples of the Iron Ore Obtained from Different Drifts and Levels of the Ore-Field.

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The first step in the chemical examination of an iron ore is the quantitative determination of its constituent elements. For an accurate estimation of iron in samples of iron ore, both before and after beneficiation, a procedure was worked out and described in a previous communication[1] on the calibration of the X-ray fluorescence spectrometer. The procedure was based essentially on the dilution of the sample (by a factor of ten) with calcium carbonate and the introduction of known quantities of cobalt as an internal standard. The present paper describes the application of the X-ray method, as well as of the standard chemical methods, to the analysis of the various random and representative samples of iron ore obtained from different "drifts" and levels of the Kalabagh ore-field.

Preliminary Examination of Hand-Picked Random Samples

For the quantitative chemical estimation of iron in various ore samples, the standard volumetric method using potassium dichromate as the titrant and diphenylamine as an internal indicator was employed.[2] An important advantage of this method lies in the fact that estimations based on it are least disturbed by the presence of interfering elements such as zinc, aluminium, manganese, nickel, cobalt and chromium. Since preliminary qualitative X-ray and chemical analyses of the iron ore under study had shown that it contains a fairly high percentage of aluminium with traces of chromium (cf. Fig. 1), this method of analysis was preferred as the one most suitable for the iron ore samples under study.

The first authentic sample of Kalabagh ore examined in the course of this study was from Mr. Abdul Karim's lease. This particular lease of iron-bearing ore extends over a length of 2 miles, constituting a small portion of 60-mile long stretch of ore body, extending on either side of the Indus river, and commonly referred to as the Kalabagh ore fields. This lease is located 4 miles from Kalabagh and is the most easily accessible area in this belt (Fig. 2(a)). It appears that the ore in this area is somewhat richer than average in iron content, and a hand-picked sample, received through the courtesy of Mr. Abdul Karim, had the reddish appearance corresponding to a rich hematitic ore. In order to find out the important metals present in the ore, a general qualitative analysis of the ore sample was carried out with the X-ray fluorescence spectrometer. Two repeats of this spectrometric record, taken on the most sensitive range of the spectrometer, are reproduced in Fig. 1, and they show in addition to iron the presence of small quantities of titanium, chromium, zirconium and strontium. With the help of the semi-quantitative calibration curve (Part I, Fig. 1), their percentages were estimated at 1.5, 0.5, 0.1 and 0.1 respectively. The elements below atomic number 22 cannot be readily detected, because their characteristic X-rays are strongly absorbed in the air.

The iron content of this sample of the ore was then quantitatively determined by the chemical and the X-ray methods, and it was found to be nearly 54%. This high iron content would seem to indicate that the sample is mainly hematite, in agreement with its reddish colour and friability. Since it was known from previous work [3,4] that the average iron content of the ore in the Kalabagh area, taken as a whole, is below 40%, this sample was evidently much richer than the average. Although a considerable amount of useful information was later obtained from the beneficiation and microscopic study of this particular sample, it was thought necessary for the proper investigation of the ore to obtain at this stage a set of fully representative samples from the ore-field, using proper sampling methods.

Sampling of the Main Iron-Bearing Vein in the Ore-Field

For this purpose, a survey of the main ore-body was undertaken, and nearly two-thirds of

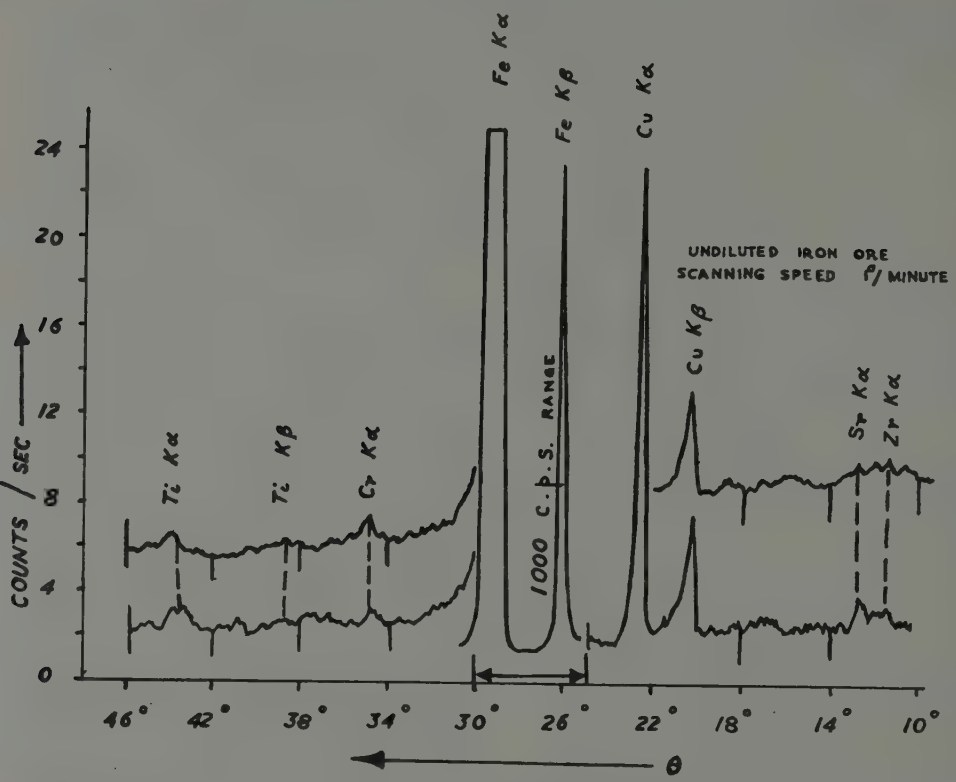

Fig. 1.—X-ray spectrometer record of rich ore sample from the Kalabagh area, showing traces of titanium, chromium, strontium and zirconium. The record from 25.5° to 30° is taken with a very much reduced sensitivity, and the rest of the record has been repeated with an upward shift of the background zero.

the entire ore-field was explored. It appeared that the major area upon which the iron mining programme can be established is the Kuch-Khartop area, which is presently being developed by the Pakistan Industrial Development Corporation and is contiguous with Mr. Abdul Karim's lease referred to above. There is nearly 2750 yards of exposed outcrop in the Kuch area and another 1750 yards of outcrop in the Khartop area. (A conservative estimate made by Dr. E.R. Gee, Director, Geological Survey of Pakistan, puts the ore reserve in this area at over 7 million tons[5]). Fig. 2(a) gives a sketch of the Kuch-Khartop area, which is easily accessible and is located approximately 6 miles from the rail-road sidings at Kalabagh, and 5 miles from the Indus river. There is an elevation of about 1000 ft. in the 5 mile distance from the river, and a motorable road can connect the actual ore site with the railway siding. A mineral water source flowing at the rate of 500 litres per minute is available nearby. It thus appeared to be an easily workable mining site, and representative samples suited for ore-dressing were therefore collected from this area, an elevation of which is shown in Fig. 2(b).

For obtaining the representative samples, the easily workable area of the ore-body was selected, its outer fringes being set by an estimated lower limit of 20% iron content. The outcrop from which the samples were collected was roughly 2-mile long and provided for a 7-foot square tunnel to be driven into it, the tunnel being entirely in the ore-bed. This criterion is quite important because it eliminates : (a) the waste-rock problem and (b) support by timbering, which is not necessary so long as the drifts remain in the ore-bed.

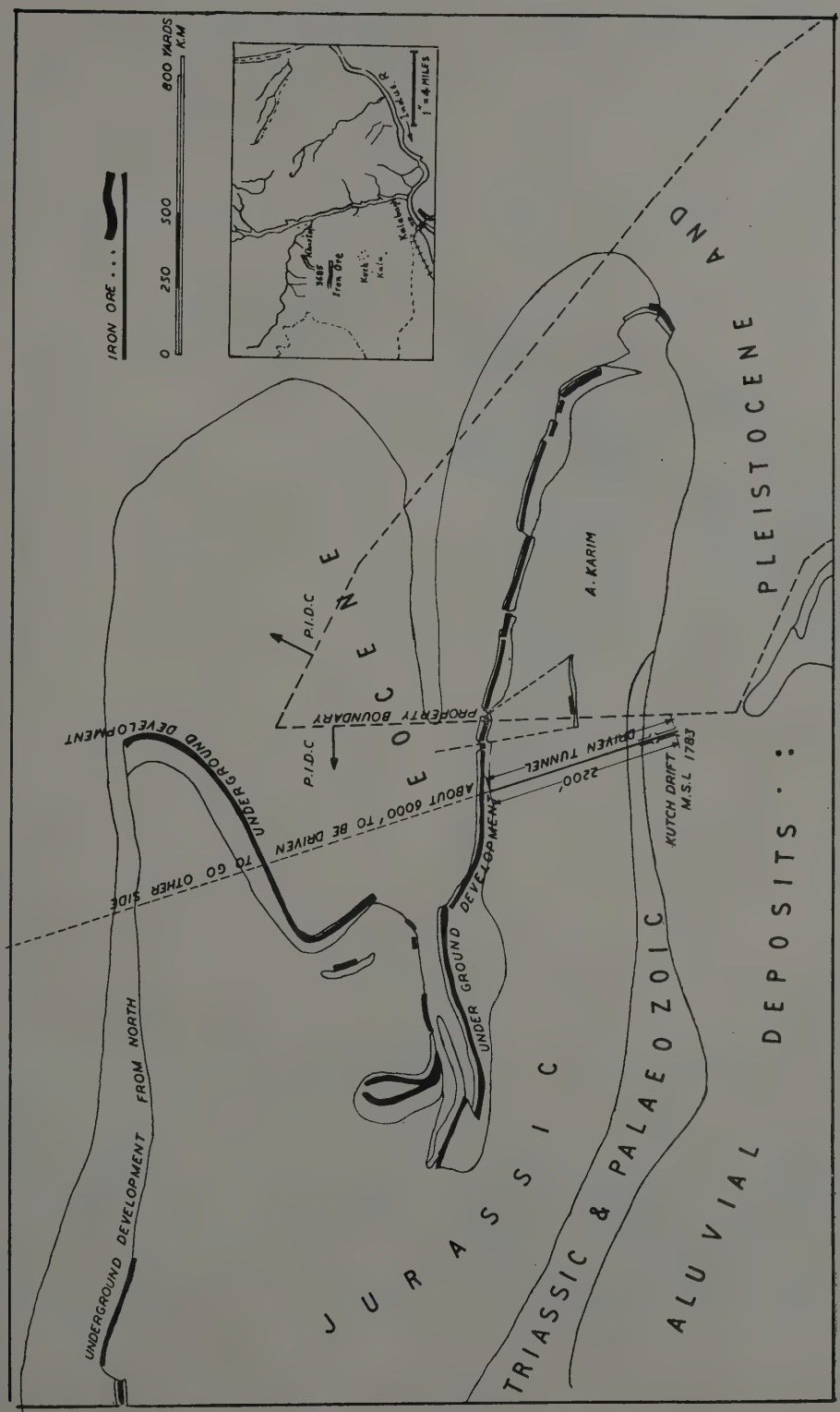

Fig. 2(a).—Sketch of the Kutch-Khartop area of the Kalabagh ore fields.

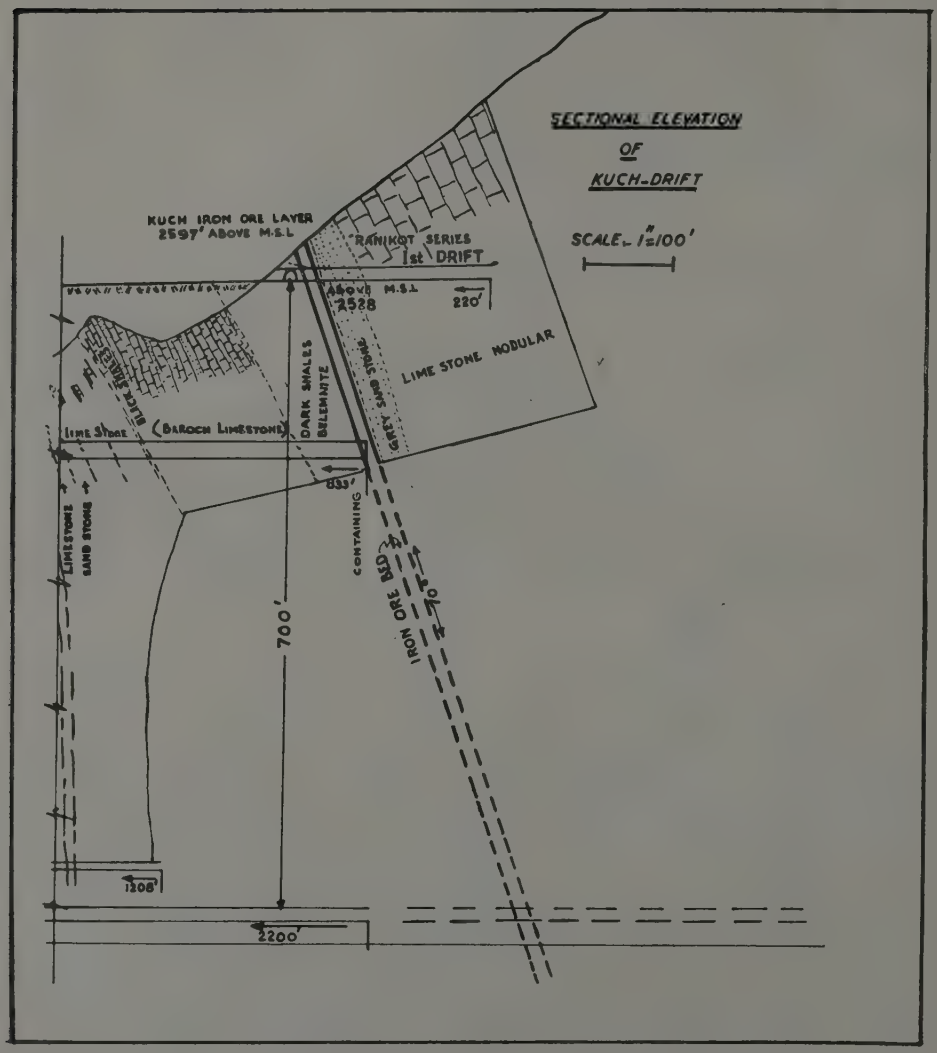

Fig. 2 (b).—An elevation of the area showing the main iron-bearing seam and two of the mine "drifts".

The sampling of the ores from individual levels was carried out by the "Breast sampling" technique, so designed as to simulate the actual production conditions and thus to get a faithfully representative sample. The sampling process can best be illustrated with reference to Fig. 3.

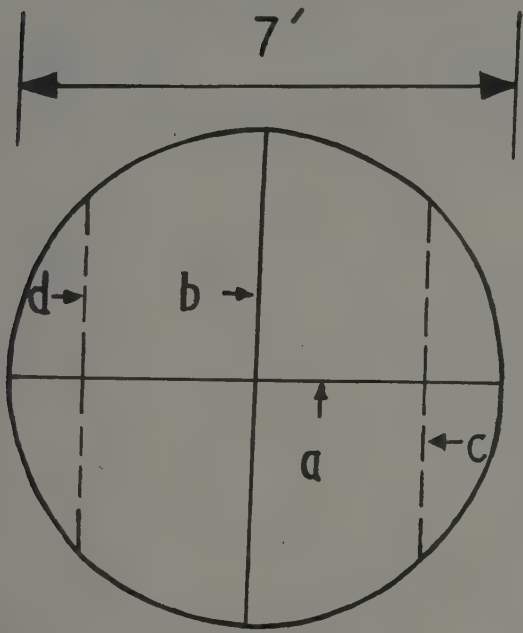

Fig. 3.—Sketch showing the mode of sampling adopted for obtaining representative samples.

From the almost circular cross-section, four individual lot samples were collected, two along the two diameters at right angles to each other (shown by 'a' and 'b' in the figure) and the other two along the two chords (shown by dotted lines 'c' and 'd' in the figure) located 'by judgement' near the periphery of the section. The four samples, thus collected, were then mixed, crushed and sectioned in order to reduce the bulk by a factor of eight and to obtain a small sample of 10 lbs. representative of this cross-section. In general, one such sample was taken from each level, and the adequacy of this sampling technique was substantiated by the fact that there was less than 1% difference between the iron contents of the mine dumps and the mean of the representative samples obtained as above (Table 1). Over a dozen such representative samples were collected from several levels spread uniformly over the working area of the outcrop (roughly 2-mile long). These samples were found to be adequate for giving definite ideas about the quality of the ore.

Analysis of Representative Samples

Each of the series of thirteen samples obtained as described above was further individually sampled to obtain still smaller (representative) samples for the analytical work. These samples, as also the mean sample from the mine dump, were then carefully analysed by chemical methods and some of the values were confirmed with the X-ray spectrometer. The mean values of iron content of each sample obtained from a number of analyses are given in Table 1.

The mean iron content of 33.5% of the ore is in agreement with the results of previous investigations,[4] and is indicative of its rather low grade. It thus becomes important to study and estimate the other constituents of the ore, for example aluminium and silicon. Accordingly, a detailed quantitative chemical analysis of three typical samples of the ore was undertaken, the three samples chosen being : (i) the mean sample containing 33.5% Fe, (ii) the poorest sample containing 22.4% Fe and (iii) the richest sample containing 39.2% Fe. The results of these analyses are given in Table 2.

TABLE 2.—DETAILED ANALYSES OF THREE TYPICAL ORE SAMPLES.

	Mean sample	Poorest sample	Richest sample
Fe ..	33.5%	22.4%	39.2%
Al_2O_3 ..	13.0%	—	11.0%
SiO_2 (total) ..	24.2%	—	15.2%
CaO ..	1.1%	2.3%	3.5%
Loss on ignition	12.6%	11.1%	12.5%
CO_2 ..	11%	6%	6%

Conclusion

This analysis brings out some significant characteristics of the ore. A comparatively high loss on ignition (roughly 12%) coupled with the fact that, on treatment with acids, the ore gives off nearly 10% carbon dioxide leads to the conclusion that an appreciable percentage of some carbonate is present in the ore. Because the percentage of calcium and other metals is very low, most of the CO_2 would be in combination

with the iron, giving nearly 26% of Fe CO_3 in the mean sample. Further, the analysis of the mean sample indicates only traces of free silica, and therefore the major portion of the silica (24.2% found in Table 2) can be expected to be combined with aluminium in the form of some alumino-silicate. (The percentages of aluminium and silicon are seen to be nearly in the right proportion to form such a compound). Both these conclusions were later fully confirmed by X-ray diffraction and mineralogical studies which showed that a considerable portion of the iron is associated with the alumino-silicate in the form of chamosite. These structural studies, which will be described in Part III of this series, are of great importance in the beneficiation and metallurgy of this iron ore, because they enable the determination of the various minerals

TABLE 1.—IRON CONTENT OF THE THIRTEEN REPRESENTATIVE SAMPLES AND THE MEAN DUMP SAMPLE.

All samples taken in the second half of October, 1957.

Sl. No.	Origin of Sample	% Fe (chemical analysis)	% Fe (X-ray analysis)
1	East limestone hill area (A. Karim)	33·5	33·4
2	Kutki stage ; Jurassic (A. Karim)..	22.4	
3	Kuch outcrop (sample taken by Geological Survey)	39·2	
4	Kuch outcrop (sample taken by Geological Survey)	26.4	
5	Limestone hill area ; main layer (A. Karim)	37·7	
6	Kuch (1st drift), West; collected at a distance of 150 metres from mouth	37.0	
7	Kuch (1st drift), West ; collected at a distance of 100 metres from the main tunnel	34·2	34·0
8	Kuch (1st drift), East; collected at a distance of 160 ft. from the main level	35·3	
9	Kuch (1st drift), East ; collected at a distance of 120 metres from the mouth	34·7	
10	Kuch (1st drift), East air level ; collected at a distance of 20 metres from the opening ; thickness of iron layer = 10 ft.	29.2	
11	Kuch (1st drift), East air levels ; 90 meters across the dip from foot wall to hanging wall *i.e.*, 0-9 ft.	31·4	
12	Kuch (1st drift), West higher level ; collected at 365 ft. from its mouth ; thickness of iron layer = 8 ft.	38.4	38.4
13	Kuch (1st drift), West higher level ; collected at 450 ft. from mouth ; thickness exposed in the mine = 6 ft. 4 inches, actual thickness being more	36.9	
14	Mean of 13 samples	33·4	
15	Mean dump sample	33·5	

constituting the ore and the distribution of iron among them.

Acknowledgements

The authors are indebted to Chaudhury Abdul Karim and to the P.I.D.C. establishment at Kalabagh for their willing co-operation in collecting the samples, to Mr. Asrarullah, Senior Geologist, Pakistan Geological Survey, for help in the general survey of the ore-field and collection of some of the samples, and to Dr. M.M. Qurashi for guidance in the X-ray measurements.

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STUDIES IN THE INFLUENCE OF LONG-CHAIN PHENOLIC ADDITIVES ON THE VISCOSITY OF MINERAL OILS

Part II.—Derivation of a Generalized Law for the Viscosity Depression in the Bhilawanol Series

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Introduction

In Part I of this paper,[1] some results were presented on the depression of viscosity produced in straight mineral oils by the addition of various proportions of bhilawanol and its monomethyl ether. A preliminary analysis of the curves for viscosity against concentration in these two cases, taken in conjunction with the results of earlier work by Mathur et al.,[2] indicated that the viscosity depression does not fall abruptly on methylation but appears to be a uniform function of the viscosity of the products. Further data in this field have now been obtained on dimethoxybhilawanol (in which both hydroxyls are converted into inactive OCH_3 groups), and, on the basis of all the data obtained so far, it is shown that the viscosity depression is correlated with the viscosity of the resinol (or its derivative) rather than with the number of OH groups. An attempt is made to derive the form of the function describing the dependence on viscosity, and further analysis leads to the setting up of a function, ψ, of the viscosity such that $\Delta\psi = (\psi_{expt} - \psi_{ideal})$ defines a function of concentration that is identical for all the compounds of the bhilawan series as well as for cashew-shell liquid.

Experiments with Dimethoxybhilawanol

Dimethoxybhilawanol was prepared according to the method described in the literature and a pale yellow product, whose colour does not unlike bhilawanol deepen on standing, was obtained. Its viscosity was measured with a U-tube viscometer of the British Standard pattern, held vertically in a water-bath kept at a temperature of 40.0°±0.05°C., and was found to be 5.05_2±0.01 centistokes. A mineral oil of nearly the same viscosity was prepared by blending two oils of viscosities 3.1 centistokes and 15 centistokes respectively (at 40°C.) in the ratio of 7 to 3. The viscosity of the blended oil at 40.0°C. was measured in the same viscometer, and was found to be 4.90_2±0.01 centistokes. This was considered close enough to the dimethyl product for the present experiment, since a correction can be applied for the difference, as discussed later in this paper.

Dimethylbhilawanol was mixed in various proportions with the blended mineral oil by weighing out appropriate quantities in a tall, covered weighing bottle. The two constituents were mixed by thorough shaking and then sufficient time was allowed for all the air bubbles to clear. The mixture was transferred into the viscometer by means of a pipette and a drawn-out filling tube so as to keep the upper portion of the viscometer tube dry. In view of the small quantities of the sample available, a semimicro-viscometer made in this laboratory was used in these experiments. The viscometer was supported vertically in a controlled temperature bath and had drying tubes connected to its ends to prevent the entry of moisture. Four to five readings of the time of flow concordant to ½% were taken and their mean was used to calculate the viscosity by means of the formula

$$\nu = At - B/t = At\left(1 - \frac{B/A}{t^2}\right),$$

where the values of the constants A and B had previously been determined by measuring the flow times of 40% sugar solution and distilled water at temperatures of 30°C. to 50°C. (cf. the graph of Fig. 1, which gives A=0.191±0.001, and B=0.35±0.02). The final accuracy of the times of flow was estimated to be of the order of

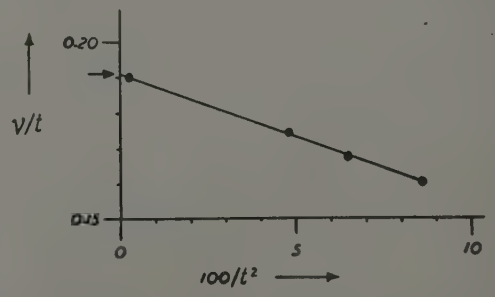

Fig. 1.—Calibration of semi-micro viscometer: linear graph for apparent viscometer constant, ν/t, against $100/t^2$.

*This communication is based in part on a thesis submitted by one of us (Z.R) to the University of Karachi for the M.Sc. degree.

0.2% or better, so that the relative accuracy of the various measurements of viscosity with this instrument will also be the same, which corresponds to 0.01 centistokes in the case of dimethoxybhilawanol and its mixtures with mineral oil. Viscosity measurements were made with mixtures, whose composition was selected so as to cover the curve in a uniform manner. The experimental results are collected in Table 1, and the graph for viscosity against wt% dimethoxybhilawanol is drawn in Fig. 2, lower curve, which clearly

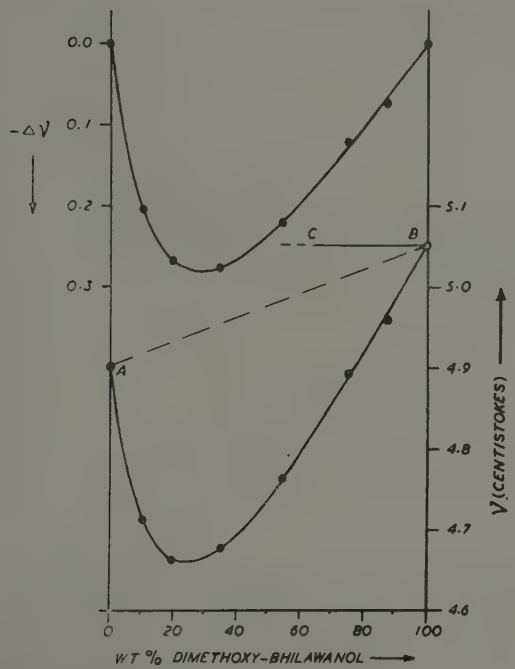

Fig. 2.—Graphs for viscosity of mixtures of dimethoxybhilawanol with mineral oil; bottom, uncorrected curve, and top, corrected depression, $-\Delta\nu$.

shows the dip in the middle of the curve. It is, however, necessary at this stage to apply a correction for the small difference in viscosity between the oil and the dimethoxybhilawanol. On the assumption of "ideal" behaviour, two theoretical relations for the viscosity of a solution of constituents 'A' and 'B' in molar proportions x_A and x_B have been proposed[3] *viz.*

$$\varphi \text{ ideal} = x_A \varphi_A + x_B \varphi_B \quad (1)$$

$$\text{and } \ln \varphi \text{ ideal} = x_A \ln \varphi_A + x_B \ln \varphi_B \quad (2)$$

where the fluidity, φ, is the reciprocal of the dynamic viscosity, η. It can be shown that when φ_A and φ_B differ by only a few percent,* both these relations are approximated to by

$$\eta \text{ ideal} = x_A \eta_A + x_B \eta_B, \quad (3)$$

which can be replaced by $\nu \text{ ideal} = y_A \nu_A + y_B \nu_B$, where y_A and y_B are the proportions by volume or weight of A and B, provided the molecular weights and densities of A and B are not very different. Thus the viscosity of the ideal solution of the mineral oil and dimethoxybhilawanol would be given by the straight line AB joining the points for the two pure constituents in Fig. 2. (The required corrections would then be given by the departure of this line from the horizontal line BC). These ideal calculated values are given in column 3 of Table 1, and the corrected viscosity depressions, $\Delta\nu$, are given in column 4 while the corrected graph is drawn in the upper half of Fig. 2. This graph has a minimum at 30% of dimethoxybhilawanol, and is seen to possess the essential characteristics of the previously obtained graphs for bhilawan shell liquid, bhilawanol, and monomethoxybhilawanol. It is necessary to note here that, because there are no hydroxyl groups left in dimethoxybhilawanol, the observed viscosity depression is to be attributed to the residual polar character of the molecule.

Discussion of the Data on the Bhilawanol Series at 40°C.

At this stage, we have available the data on the viscosity depression produced by five bhilawan products and derivatives with viscosities ranging from 370 centistokes down to 5 centistokes. The important quantities derived from the graphs for these compounds are collected together for analysis in Table 2. As noted in Part I of this paper, the two indices I_1, I_2, which were used as measures of the viscosity depression, are neither constant nor do they show a precipitous drop on methylation, whether partial or complete. Simple correlation with the number of hydroxyl groups is further upset by the fact that bhilawan shell liquid (with only two OH groups) has considerably higher values of the indices than bhilawanol. Rather, the indices appear to vary uniformly with the viscosity of the product investigated and it is desirable to determine the precise law of this variation. Since inspection shows the possibility of a proportionality with some power of the viscosity, ν, a logarithmic plot is indicated. Accordingly the logarithms of ν, $-(\partial\nu/\partial x)_{x=0}$, $-(\Delta\nu_m/x_m)$, $-\Delta\nu_m$, and $\bar{\nu}$ have been calculated in Table 3, $\bar{\nu}$ being the mean of the original and the lowered values of the viscosity. Fig. 3

*In fact it can be shown (*see* Appendix to present paper) that for mineral oils (known to obey equation 2 fairly well) with viscosities differing by 3% as in the present case, the maximum difference between equations 2 and 3 is nearly 0.01 % of the viscosity.

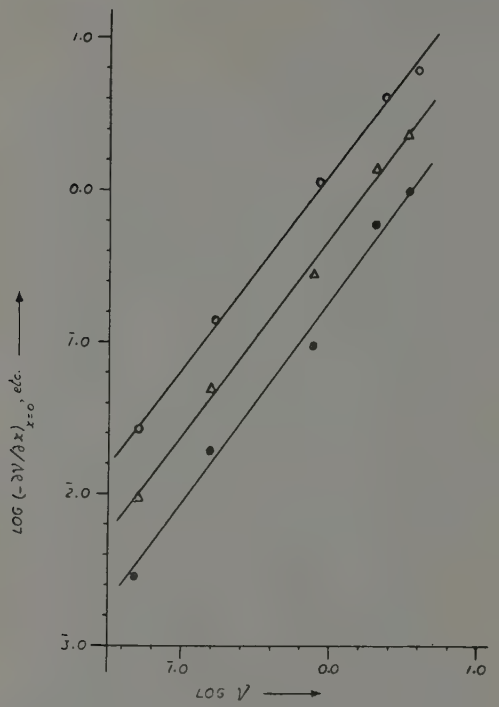

Fig. 3.—Linear logarithmic graphs showing the dependence of the viscosity depression on the viscosity of the compounds. Hollow circles, log $-(dv/dx)_{x=0}$ against log v ; triangles, log $(-\Delta v/x_m)$ against log $\bar{v}$; solid circles, log $(-\Delta v_m)$ against log $\bar{v}$.

shows plots of log $(-\partial v/\partial x)_{x=0}$ against log v (hollow circles) and log $(-\Delta v_m/x_m)$ against log $\bar{v}$ (triangles). There result two acceptable straight lines that are sensibly parallel to each other, the slopes being 1.29_5 and 1.30_5, respectively. The mean is $1.30_0 \pm 0.005$, which shows that both $(-\partial v/\partial x)_{x=0}$ and $(-\Delta v_m/x_m)$ are very nearly proportional to $v^{1.30}$. However, the corresponding plot of log $(-\Delta v_m)$ against log v (solid circles) has a slope of 1.338 ± 0.02, indicating that $\Delta v_m \propto (\bar{v})^{1.34}$. Since this last value does not depend on the composition for maximum depression, it is given greater weight, and the best value of the index for the curve as a whole may be taken as 1.33 ± 0.01. We can now write

$$-(\partial v/\partial x)_{x=0} = \text{Constant} \times v^{1.33}, \qquad (4)$$

from which it follows that

$$\frac{\partial}{\partial x}(v^{-0.33}/0.33) = -v^{-1.33}\,\partial v/\partial x = \text{Constant}, \qquad (5)$$

with the value 1.40 for the bhilawanol series. Similarly we get

$$\Delta\,(v^{-0.33}/0.33)_{max} = \text{Constant} \qquad (6)$$

with the value 0.20 for the bhilawanol series.

It is well to note here that, although the concentration, x, has been expressed as parts by weight in our measurements, it is in fact very close to the corresponding mole fraction, as can be seen by comparing the molecular weights of the pairs of liquids constituting the binary mixtures under investigation (Table 2). The molecular weights of the oils were determined by the cryoscopic method.

Further Generalization into a Simple Law

The above results suggest the advisability of using a function $\psi_n = (v^{-n} - 1)/n$ for further elucidation of the phenomena involved in the viscous behaviour of non-ideal solutions. The advantage of selecting this type of function is that

(a) for $n=1$, $\psi_{n=1} = \psi_1 = 1/v - 1$, so that

$$\Delta\psi_1 = \Delta(1/v),$$

(b) for small n, $\psi_n = \dfrac{v^{-n} - 1}{n}$

$$= \frac{1}{n}\exp(-n \ln v) - \frac{1}{n} = \ln 1/v + \frac{n}{2}(\ln 1/v)^2,$$

$$\text{so that} \quad \Delta\psi_{n \to 0} = \Delta(\ln 1/v).$$

Thus (ignoring the small variation of ρ in the relation $v = \eta/\rho$) the values '1' and '0' of the index 'n' make the function ψ_n correspond to the two functions, $\varphi = 1/\eta$ and $\ln \varphi = \ln 1/\eta$ (cf. equations 1 and 2) that have at different times been supposed to vary linearly with the concentrations of the two components of an ideal solution[3]. It is therefore significant that the above analysis of the viscosity depression, *i.e.*, the departure from ideal behaviour, leads to the conclusion (equations 5 and 6) that $(\partial\psi_{0.33}/\partial x)_{x=0}$ and $(\Delta\psi_{0.33})_{max}$ are constant. This means that the curves for $\Delta\psi_{0.33}$ against concentration, x, should be identical for all the substances of the one series listed in Table 2, from which it can be inferred that, for an analysis of the viscosities of solutions, the function $\Delta\psi_{0.33}$ is of considerable importance.* The values of

* It is worth noting here that if the correction in Table 1 is entirely neglected, the maximum error in Δv_{max} is 0.075, which would correspond to an alteration of only 0.01 in the mean slope of the straight line graphs of Figure 3, and therefore in the index 0.33 found for the function ψ_n .

TABLE 1.—VISCOSITY OF MIXTURES OF DIMETHOXYBHILAWANOL WITH MINERAL OIL.

wt% Dimethoxybhilawanol	Measured viscosity (centistokes)	Calculated viscosity for "Ideal" solution (centistokes)	Corrected depression $= \Delta\nu$ (centistokes)
0.0	4.902	4.902	—0.000
10.2	4.712	4.917	—0.205
19.7	4.662	4.932	—0.270
35.0	4.677	4.954	—0.277
54.6	4.763	4.984	—0.221
75.1	4.893	5.015	—0.122
87.2	4.959	5.032	—0.073
100.0	5.052	5.052	—0.000

TABLE 2.—SYNOPSIS OF DATA ON DEPRESSION OF VISCOSITY FOR THE BHILAWAN SERIES (x = PARTS OF SUBSTANCE BY WEIGHT).

Workers	Substance	Viscosity at 40% C. (stokes)	Density (g./ml.)		Molecular wt.		$I_1 = \frac{-1}{\nu}\left(\frac{\delta\nu}{\delta x}\right)_{x=0}$	$I_2 = \frac{-1}{\nu}\frac{\Delta\nu_m}{x_m}$	Ratio I_2/I_1
			Substance	Mineral oil	Substance	Mineral oil			
Mathur et al.	Bhilawan (a) ..	3.70	0.975	0.940	—	—	1.65/part	0.70/part	0.41
	Shell liquid (b) ..	2.22	—	—	—	—	1.9/ ,,	0.66/ ,,	0.36
Qurashi	Bhilawanol ..	0.801	0.954	0.905	316	360	1.35/ ,,	0.36/ ,,	0.48
Qurashi	Monomethoxybhilawanol	0.162	0.90	0.875	330	320	0.86/ ,,	0.28/ ,,	0.33
This paper	Dimethoxybhilawanol ..	0.0505	0.91	0.850	344	280	0.55/ ,,	0.19/ ,,	0.36
								Mean =	0.39 ± 0.02

TABLE 3.—VALUES OF LOG $\left(-\frac{\partial\nu}{\partial x}\right)_{x=0}$ ETC., FOR COMPOUNDS OF THE BHILAWAN SERIES (ν TAKEN IN STOKES).

Substance	$\left(-\frac{\partial\nu}{\partial x}\right)_{x=0}$	$\log\left(-\frac{\partial\nu}{\partial x}\right)_{x=0}$	$\log\nu$	$-\frac{\Delta\nu_m}{x_m}$	$\log\left(-\frac{\Delta\nu_m}{x_m}\right)$	$\log\bar{\nu}$	$\log(-\Delta\nu_m)$
Bhilawan (a) ..	6.10	0.786	0.657	2.25	0.353	0.507	$\bar{1}.987$
Shell liquid (b) ..	4.10	0.613	0.347	1.34	0.128	0.284	$\bar{1}.771$
Bhilawanol ..	1.10	0.042	$\bar{1}.904$	0.275	$\bar{1}.440$	$\bar{1}.878$	$\bar{2}.974$
Monomethoxy-bhilawanol ..	0.139	$\bar{1}.144$	$\bar{1}.210$	0.048	$\bar{2}.682$	$\bar{1}.184$	$\bar{2}.282$
Dimethoxy-bhilawanol	0.0275	$\bar{2}.439$	$\bar{2}.703$	0.0094	$\bar{3}.974$	$\bar{2}.690$	$\bar{3}.451$

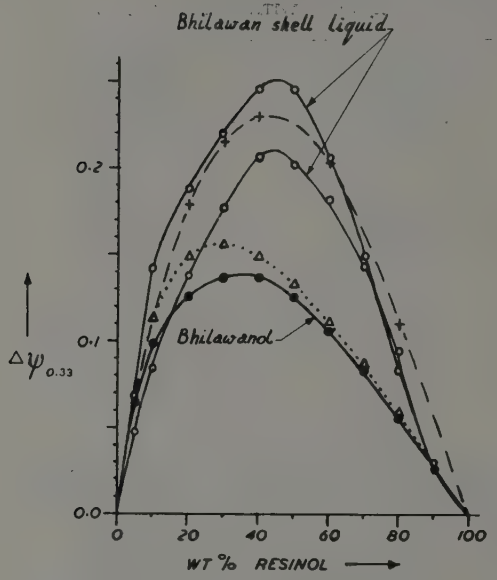

Fig. 4 (a).—Graphs of $\Delta\psi_{0.33}$ against concentration for the five bhilawanol products.

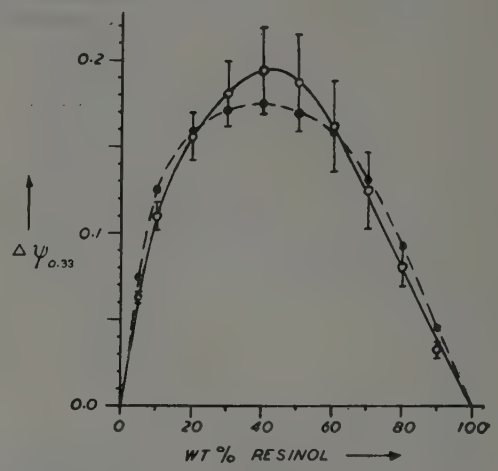

Fig. 4 (b).—Plot of mean values of $\Delta\psi_{0.33}$ for the five bhilawanol products (full line) compared with the corresponding curve for cashewshell liquid (broken line).

$\Delta\psi_{0\cdot33}$ for the five products in Table 2 are calculated below for x=0.05, 0.1, 0.2, 0.3, ... etc. in Table 4(a), and the corresponding graphs are drawn in Fig. 4(a). All these graphs are seen to agree closely with each other in the region of small concentration of the resinol (or its derivative), almost upto the point of maximum viscosity depression. The last rows of Table 4(a) give the mean values of $\Delta\psi_{0\cdot33}$ for the bhilawanol series, together with the standard deviations of the means. These mean values are plotted in Fig. 4(b), where the deviations are shown by short vertical lines through the points.

Applications and Discussion

As an application of the above generalization, we consider the data obtained by Mathur at al.[2] on cashew shell liquid, whose principal constituent, anacardol $[C_6H_4(OH)C_{15}H_{27}]$ is similar to bhilawanol, except that it contains only one hydroxyl group, instead of the two in bhilawanol, and therefore corresponds in a sense to monomethoxybhilawanol although its viscosity (150 centistokes) is nine times greater. Table 4(b) gives the values of viscosity taken from the data of Mathur et al. on mixtures of cashew shell ilquid with three different mineral oil blends at 40 °C. The mean values of viscosity and $\Delta\psi_{0\cdot33}$ are given in the last two rows of the table, and the corresponding curve is drawn in Fig. 4(b) with a broken line. It is evident that the $\Delta\psi_{0\cdot33}$ curve for cashew shell liquid agrees within the limits of experimental error with the mean curve for the bhilawanol series. This agreement confirms the earlier conclusion that the viscosity depression is correlated with the viscosity of the compounds rather than with the number of active OH groups, because the actual viscosity depression for cashew shell liquid is ten times that obtained with the similar (monohydroxylic) compound monomethoxybhilawanol.

Finally, in Table 4(c) a comparison of the standard deviation of any one curve from the means is given for the bhilawanol series and for cashew shell liquid. On the whole, these deviations are proportional to $\Delta\psi_{0\cdot33}$, so that the overall mean of these standard deviations, when expressed as a percentage of $\Delta\psi_{0\cdot33}$, in the last row of Table 4(c) is nearly constant at 22%. It follows that the measurement of either $(\partial\psi_{0\cdot33}/\partial x)_{x=0}$ or $(\Delta\psi_{0\cdot33})_m/x_m$ is equally representative in any given case. Now the determination of the first of these two quantities involves uncertainties inherent in drawing a tangent to a curve at the origin (x=0), while the second is uncertain due to the usual indefiniteness in the value of x for the maximum. The determination of $(\Delta\psi_{0\cdot33})_{max}$, on the

TABLE 4(A).—VALUES OF $\Delta\psi_{0\cdot33}$ FOR BHILAWAN SHELL LIQUID, BHILAWANOL, AND ITS DERIVATIVES.

Substance \ 100x = wt%	0	5	10	20	30	40	50	60	70	80	90	100
Bhilawan shell liquid (a) ..	.000	.048	.084	.13$_8$	.177	.207	.202	.18$_2$	.14$_4$	.09$_5$	.027	.000
Bhilawan shell liquid (b) ..	.000	.06$_9$	.14$_2$	.188	.220	.24$_6$	.24$_6$	.20$_6$	.15$_0$	.08$_4$	.03$_0$	.000
Bhilawanol ..	.000	.06$_5$	.09$_9$	.12$_6$	.137	.137	.126	.10$_6$	.083	.05$_6$	.02$_0$	.000
Monomethylbhilawanol	.000	.06$_3$	.11$_1$	.17$_9$	.21$_6$	.23$_0$	(.227)	.204	(.163)	.11$_1$	(.055)	.000
Dimethylbhilawanol ..	.000	.07$_2$	.11$_3$	.149	.156	.149	.13$_3$	.11$_1$	.086	.05$_8$	.02$_9$	.000
Mean ..	.000	.063	.11$_0$	.156	.181	.194	.187	.162	.125	.08$_1$	.03$_3$	.000
Std. dev. of mean ..	—	±.005	±.008	±.014	±.018	±.025	±.028	±.026	±.022	±.011	±.005	—

TABLE 4(B).—VALUES OF VISCOSITY (IN STOKES) AND OF $\Delta\psi_{0\cdot33}$ FOR CASHEW SHELL LIQUID.

Mixture with.... \ 100x = wt%	0	5	10	20	30	40	50	60	70	80	90	100
Oil blend (1) ..	1.14$_0$	1.03	0.97	0.94	0.93	0.92	0.91$_5$	0.93	0.95	1.00	1.05$_5$	1.12$_2$
Oil blend (2) ..	1.13$_8$	1.06$_5$	1.01	0.97	0.95$_5$	0.95	0.95$_5$	0.96$_5$	0.99	1.02$_5$	1.07$_5$	1.12$_2$
Oil blend (3) ..	1.12$_5$	1.06	1.00$_5$	0.98	0.97	0.97	0.98	0.99	1.01$_5$	1.04$_5$	1.08$_5$	1.12$_2$
Mean viscosity ..	1.13$_4$	1.05$_2$	0.99$_5$	0.96$_3$	0.95$_2$	0.94$_7$	0.95$_0$	0.96$_2$	0.98$_5$	1.02$_3$	1.07$_2$	1.12$_2$
Mean $\Delta\psi_{0\cdot33}$ ..	0.000	0.074	0.125	0.159	0.171	0.175	0.169	0.158	0.131	0.093	0.046	0.000

TABLE 4(C).—STANDARD DEVIATIONS OF THE VARIOUS CURVES.

100 x :—	0	5	10	20	30	40	50	60	70	80	90	100
Std. deviation of the individual curves (1) Bhilawan series	—	0.010	0.016	0.029	0.037	0.050	0.057	0.052	0.045	0.022	0.010	—
Std. deviation of the individual curves (2) Cashew	—	0.020	0.023	0.020	0.020	0.024	0.029	0.026	0.029	0.020	0.014	—
Mean ..	—	0.015	0.020	0.024	0.029	0.037	0.043	0.039	0.037	0.021	0.012	—
Mean (as % of mean $\Delta\psi_{0\cdot33}$)	—	22	17	15	17	20	24	24	29	24	29	—

other hand is subject to neither of these two errors, and is probably the best quantity to use, especially over small ranges of variation of the viscosity, because it can be determined very accurately by taking measurements with two or three compositions in the vicinity of the composition for maximum $\Delta\psi$.

The foregoing results have been obtained with phenolic compounds having a long $C_{15}H_{27}$ side chain, containing two double bonds. In order to establish these results on a firm basis, it is desirable to extend the experiments to phenolic compounds with shorter chain lengths and also to study the effect of the number and position of the double bonds in this side chain. This work is in progress and the results on the allyl series of phenolic compounds will be reported soon.

Acknowledgements

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Appendix

Accuracy of the Correction for Difference of Viscosity between the Two Constituents

We consider the equation $-\ln\eta = \ln\varphi = x_A \ln\varphi_A + x_B \ln\varphi_B = -x_A \ln\eta_A - x_B \ln\eta_B$, (2)
because it is the more nearly correct one for non-polar liquids. If we replace this by the approximate equation $\eta' = x_A\eta_A + x_B\eta_B$ (3)
then the error caused by this approximation is

$$\eta' - \eta = (x_A\eta_A + x_B\eta_B) - \exp[x_A\ln\eta_A + x_B\ln\eta_B]$$
$$= \eta_A + x_B(\eta_B - \eta_A) - \exp[\ln\eta_A + x_B(\ln\eta_B - \ln\eta_A)]$$
$$= x_B(\eta_B - \eta_A) - \eta_A[\exp(x_B\ln\eta_B/\eta_A) - 1]$$
$$= x_B(\eta_B - \eta_A) - \eta_A[(\eta_B/\eta_A)^{x_B} - 1)]$$
$$= x_B(\eta_B - \eta_A) - x_B(\eta_B - \eta_A) + \frac{x_B(1-x_B)}{2}\frac{(\eta_B-\eta_A)^2}{\eta_A} + \ldots$$
$$= \eta_A \frac{x_B(1-x_B)}{2}\left(\frac{\eta_B - \eta_A}{\eta_A}\right)^2$$
$$+ \text{higher powers of } (\eta_B - \eta_A)/\eta_A$$

This expression has its maximum value for $x_B = 1 - x_B = \frac{1}{2}$,
so that the maximum fractional error is given by

$$\left(\frac{\eta' - \eta}{\eta}\right)_{max} \simeq \frac{\frac{1}{2}\times\frac{1}{2}}{2}\left(\frac{\eta_B-\eta_A}{\eta_A}\right)^2 = \frac{1}{8}\left(\frac{\eta_B - \eta_A}{\eta_A}\right)^2,$$

which is equal to 0.011% for $(\eta_B - \eta_A)/\eta_A = 3\%$. Since the usual experimental errors in the measurement of viscosity are seldom much less than 0.3%, it can be seen from the above equation that the approximate correction formula (3) is applicable even when $(\eta_B - \eta_A)/\eta_A$ is as large as 15%.

FRACTIONATION AND PREPARATION OF FATTY ACIDS AND ESTERS FROM NATURAL MIXTURES WITH THE HELP OF UREA COMPLEXES

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Introduction

The preparation of concentrates of unsaturated fatty acids (or their methyl esters) is an important and basic problem in fat chemistry. Vacuum fractionation, low temperature crystallization and cold storage are usually employed for fractionation of fatty acids, but in countries in which there are no such facilities, the processes involving urea complex formation are indispensable. Schlenk and Holman[1] were apparently the first workers to employ urea complexes in the preparation of purified methyl oleate from olive oil. In order to separate the saturates, these investigators used a stepwise addition of urea which was designed to remove successive 10% portions of olive oil methyl esters as urea complexes. Then they took out one bulk portion representing only methyl oleate. Further purification was accomplished by vacuum fractionation. The purpose of the present investigation was to study the possibility of using urea complex formation alone for concentrating fatty acids of different types in the natural oils, mustard, linseed, cottonseed, sesame, and castor. Initially, some preliminary experiments were conducted to obtain information on separability in mixtures of some known composition. These results were then extended to indigenous oils in order to investigate firstly the feasibilities of isolation of important fatty acids from the oils and secondly to fix optimum conditions for formation of urea complexes with reference to maximum yield and purity of fatty acids in question.

Experimental

Materials.—The methyl esters of cottonseed, linseed and castor oils were obtained by methanolysis through sodium methoxide and methyl alcohol. The acids of sesame and mustard oils were prepared by saponification and subsequent hydrolysis. Methyl oleate (I.N. (Iodine Number) 86.2) was obtained by the methods previously described.[2] Methyl linoleate (I.N., 172.0) and methyl linolenate (I.N., 259.4) were prepared by bromination and debromination methods[3] applied to sesame oil and linseed oil acids.

Apparatus and Methods.—The standard mixture (250 g.) of methyl oleate (I.N., 86.2) and linoleate (I.N., 172.0) and linoleate (I.N., 259.4) in the ratio 1 : 1 : 1, was subjected to urea complex fractionation by using 250 ml. methanol at the start under reflux and 100 g. of urea for each fraction.[4] The agitation during complex formation was carried out by a strong and heavy-duty mechanical stirrer. For equal amounts (250 g. each) of other methyl esters, the quantity of methyl alcohol remained the same while hat of urea was varied as follows : 100 g. in etach of first four fractions of cottonseed and linseed and three castor oil esters and 200 g. in the rest except the last fraction, which represented the filtrate. One hundred grams of urea were used for each of the fractions in sesame oil acids and also for first five fractions in mustard oil acids and then 50 g. for each of the remaining fractions. The urea crystals in each fraction were thoroughly washed with ethyl ether (redistilled over KOH flakes). The wash liquid was freed of solvent and the residue was added to the next proper filtrate obtained during urea complex formation. The fatty acid and ester fractions were recovered by addition of water and a few ml. of dilute hydrochloric acid and then dried over anhydrous sodium sulphate. After analysis, the requisite samples were refractionated through the usual urea complex formation. 4,[5] In case of the standard mixture (Table I), the oleate fraction was subjected to urea complex formation once, (with an equal volume of methyl alcohol per weight of oleate and urea three times its weight), the linoleate fraction four times and the linolenate fraction, six times. For other natural oil ester and acids, the oleate and oleic acid fractions were each fractionated once by the foregoing method, linoleate and linoleic acid twice, linolenate four times, and erucic acid only once. The urea crystals finally obtained from each fraction were refluxed for one hour with methyl alcohol sufficient for covering the crystals, and then cooled. The crystals were washed in all cases with ethyl ether to remove adhering alcohol and fat components. Rough estimations of linoleic and linolenic acids were made by bromination methods.[6]

Results and Discussion

Table I shows the distribution pattern of fatty acid esters of different unsaturation after urea-complex fractionation of the standard mixture (oleate : linoleate : linolenate = 1:1:1). On refractionation oleate was obtained from fraction I and II (I.N. 89.7 : ca. 96.0% pure), linoleate from IV and V (I.N., 176.4: ca. 91.0%), and

linolenate from VI and VII (I.N., 249.1 : ca. 83.0%). The experimental data of Table I on the fractionation of a standard mixture established the trends of the procedures of urea fractionation to be used in the unknown natural mixtures (Table 2.).

TABLE I.—FRACTIONATION OF STANDARD MIXTURE BY UREA COMPLEX FORMATION.

Fractions	% of total ester	I.N.	Fractions containing in major quantities of
I	12.0	96.1	Oleate
II	16.0	101.1	
III	15.0	136.7	Unknown intermediate
IV	12.8	164.0	Linoleate
V	14.6	190.8	
VI	15.7	210.4	Linolenate
VII	13.9	236.4	

Methyl esters of three natural oils used initially for urea complex formation (Table 2) gave better fractionation. In the later fractionations, acids of two oils gave good separation, but some degree of esterification of the acids with methyl alcohol necessitated saponification and hydrolysis of the each fraction to regenerate the total acids. Inspite of this difficulty, sometimes acids are found advantageous as starting materials. Table 2 shows the general picture of separation of different fat components with respect to yields and degree of unsaturation in the fractions.

Further purification of the samples in Table 2 by refractionations through urea complexes, yielded reasonably pure fatty acids and esters. Table 3 indicates the purity and yields of different fatty acids and esters after this refractionation. Such purified samples from the local resources would serve various purposes in research in our environments. Further work is in progress to study other advantages of urea-complex formation.

Acknowledgement

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TABLE 2.—IODINE NUMBER (I.N.) AND CORRESPONDING DISTRIBUTION OF THE UNSATURATES IN THE VARIOUS FRACTIONS OF OILS.

Fractions	METHYL ESTER OF						ACIDS OF			
	Cottonseed Oil		Linseed Oil		Castor Oil		Sesame Oil		Mustard Oil	
	I. N.	% of total ester	I. N.	% of total ester	I. N.	% of total ester	I. N.	% of total acids	I. N.	% of total acids
1	18.5	12.0	95.1	9.6	60.7	8.8	29.5	14.0	52.2	12.8
2	49.5	18.1	108.6	15.7	78.6	11.0	61.2	19.0	73.1	13.2
3	127.1	23.9	169.0	18.0	84.5	18.4	96.5	21.0	84.3	15.6
4	153.9	18.0	178.3	16.0	85.8	21.0	116.6	19.0	87.9	16.6
5	166.5	8.6	189.4	11.8	86.2	40.8	146.2	7.7	92.1	17.2
6	161.6	15.2	230.1	28.9			153.4	8.3	136.2	11.6
7	151.6	4.2					150.5	11.0	181.7	6.4
8									175.4	4.8
9									101.9	1.8

TABLE 3.—CHARACTERISTICS OF SAMPLES OF FATTY ACIDS AND ESTERS PREPARED THROUGH UREA COMPLEXES.

Samples (methyl esters)	I. N.	Yields : % of initial total ester (Table 2)	Sources refractionated (Table 2)
Methyl linoleate ..	167.2	11.2	5th and 6th fractions of cottonseed esters.
Methyl linoleate ..	173.2	14.6	3rd and 4th fractions of linseed esters.
Methyl linolenate ..	244.1	8.4	6th fraction of linseed esters.
(Acids)	**I. N.**	**Yields : % of total acids**	**Sources as above**
Oleic acid ..	91.2	15.6	3rd fraction of sesame oil acids.
Linoleic acid ..	174.5	10.8	5th, 6th and 7th fractions of sesame oil acids.
Erucic acid ..	73.1	16.5	2nd and 3rd fractions of mustard oil acids.
Linoleic acid ..	181.7	5.4	7th and 8th fractions of mustard oil acids.

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EXAMINATION OF RUBBERSEED OIL FOR USE IN COATING COMPOSITIONS

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Introduction

Rubberseed oil is obtained from the seeds of *Hevea Brasilieusis*, native to Brazil and extensively cultivated in many tropical regions including Malaya, Borneo, Sumatra and Ceylon. The yield of the seed is estimated at 300 lbs./acre/annum. The total area under rubber cultivation in the various rubber producing countries of the world was reported[1] to be 10,000,000 acres in 1953, so that the potential availability of seeds would be about 1.3 million tons annually, making for a total of 260,000 tons of the oil on the basis of 20% yield. As against this potential, the present world output of the oil is reported to be only 20,000 tons, corresponding to a 8% utilisation of the seeds.

There are two main reasons for this neglect of such a valuable source of oil :

(1) The seeds deteriorate rapidly on storage, yielding a dark-coloured oil with a high proportion of free fatty acids. To counteract this drawback, various methods of heat treatment have been suggested, and it is reported[2,3] that the seeds do not deteriorate and the oil extracted from heat-treated seeds can be stored for as long as two years with very little increase in free acidity.

(2) Lack of economic methods for improving the drying properties of semi-drying oils like rubberseed oil or for using them in oleo-resinous varnishes. Fatty acids obtained from semi-drying oils are no doubt favoured for the preparation of alkyd resins, but their present demand is being largely met by another semi-drying oil, namely soyabean oil. The present output of rubberseed oil appears to be mostly consumed in soap manufacture, though it has also been recommended, as an adulterant for linseed oil and as its substitute in core binders.[4]

In order to gauge the drying power of an oil for use in coatings, a drying index has been suggested[5] in the form of the sum of the percentage content of linoleic acid and double the percentage content of linolenic acid. Drying indices calculated on this basis for linseed, rubberseed, soyabean and cottonseed oils work out to be 120, 80, 68 and 45 respectively. The drying properties of rubberseed oil can therefore be regarded as being intermediate between those of soyabean and linseed oil, and it would therefore be advantageous to study its utilization in coating compositions. In view of the fact that rubber plantation has been recently started in East Pakistan, it was considered of importance to undertake a fuller investigation of the various aspects of the problems relating to the utilisation of the rubberseed in order to strengthen the economy of the plantation. The present paper deals with the results of studies in the keeping quality of the seeds and the extracted oil, both with and without heat treatment, and the utilisation of the oil for the preparation of oleo-resinous varnishes capable of giving tack-free films with the process developed for cottonseed oil[6] at the Central Laboratories. For the present study, the rubberseeds were obtained from Malaya through Messrs Chemtong Malaya Rubber Company, soon after collection.

Experimental

The seeds were found to contain 41.8% shell and 58.2% kernel, the latter containing 37% oil. The moisture content of the kernel was 7.8% by weight and 8.0% by weight in the whole seeds. The characteristic constants of the oil from the seeds as received were measured and are reported in Table I. The reported values show large variations, which are probably due to variations in age and quality of the rubberseeds.

Detailed examination showed that rubberseeds exhibit considerable variations in quality and the seeds were therefore classified according to the colour of the kernel as given in Table 2, the oil from the dark varieties having a much higher acid value than that from the light varieties.

Undecorticated seeds, without heat treatment and after heat treatment for varying periods, were stored in tin cans. At six-monthly intervals, the oil was extracted from these stored seeds using petroleum ether as a solvent and its content of free fatty acid was determined in order to estimate the rate of deterioration of the seeds. The results are reported in Table 3.

To study the storage deterioration further, the oil from the two main varieties, light and dark, was extracted and its keeping qualities were compared with the oil from the total rubberseeds during storage for about 15 months. The acid values determined at different intervals are given in Table 4.

TABLE 1.—CHARACTERISTIC CONSTANTS OF RUBBERSEED OIL.

	Present Investigation	Ref. 7	Ref. 8	Ref. 9
Specific gravity at 26°C. ..	0.9178	—	0.9245 at 15°C.	0.924—0.930 at 15°C.
Refractive index at 26°C. ..	1.4723	—	—	1.4665—1.4685 at 40°C.
Acid value	22.6	40.9	—	10—50
Iodine value (Hanus) ..	132.2	135.2	139.3	133—143
Saponification value ..	209	191.8	192.5	186—195
Unsaponifiable matter % ..	1.3	—	—	0.5—0.8

TABLE 2.—CLASSIFICATION OF RUBBERSEEDS AS RECEIVED.

Colour of Kernel		Proportion %	Oil content (on weight of kernel) %	Colour of oil	Acid value
Light	White ..	20.0	38.8	faint yellow	2.9
	Cream ..	50.0	38.5	yellow	4.6
Dark	Dirty brown ..	25.0	33.2	reddish brown	60.9
	Grey black ..	5.0	30.6	dark brown	86.2

TABLE 4.—ACID VALUES OF STORED OILS FROM THE RUBBER SEEDS.

Date of examination	Oil from light seeds (untreated)	Oil from light seeds (heat treated)*	Oil from dark seeds	Oil from total rubber seeds
5- 1-57	4.1	3.9	64.6	22.6
16- 1-57	4.2	4.1	66.8	23.0
16- 2-57	4.4	4.2	76.9	24.6
17- 4-57	4.6	4.5	89.6	30.4
16- 6-57	5.1	5.2	96.8	35.2
14-10-57	6.2	7.3	†	
31- 3-58	7.2	23.0		42.7

* Kernels heated at 100°C. for one minute.

† Acid value remains constant, but free fatly acids keep depositing.

It was observed that, oil from heat treated kernels showed a slow increase in viscosity from 42 centistokes at 25 °C. to 60 centistokes at 25 °C. during the first nine months and thereafter a sharp increase, the viscosity after fourteen months' storage being found to be 450 centistokes at 25 °C. During this latter period, the acid value also showed a sharp increase, the two effects indicating polymerization of the oil. On the other hand, the oil from untreated kernels retained the original viscosity on storage. Separation of free fatty acids started in the oil from the dark varieties after storage of three months, and after fifteen months the iodine value of the supernatant oil had increased to 135.5. There was no separation of free fatty acids in the other varieties.

A process developed at the Central Laboratories for preparing tack-free coatings (oleo-resinous) from cottonseed oil (iodine value 107), has now

TABLE 3.—ACID VALUES OF OILS FROM STORED SEEDS WITH AND WITHOUT HEAT TREATMENT.

Period of storage	Untreated	Seeds heated at 100 °C. for (in minutes)		
		5	10	20
Initial	22.5	—	—	—
6 months	82.5	35.6	33.8	34.2
12 ,,	—	38.6	37.9	38.0
18 ,,	—	46.8	42.7	43.3

TABLE 5.—COMPARATIVE SCRATCH TEST OF VARNISH FILMS.

Sl. No.	Oil length (gallons)	Load in grams	
		Rubber-seed varnish	Linseed varnish
1	15	250—260	250—260
2	25	300—310	300—310
3	35	300—310	310—15

TABLE 6.—COMPARATIVE WATER RESISTANCE OF VARNISH FILMS.

Sl. No.	Oil length	Oil used	Water-resistance of films				
			1 hr.	2 hrs.	4 hrs.	24 hrs.	48 hrs.
1	15	Rubberseed ..	OK	OK	V. Sl. H.	Sl. H. (D : 2 hrs.)	W (D : 16 hrs.)
	15	Linseed ..	OK	OK	OK	Sl. H. (D : 2 hrs.)	W (D : 14 hrs.)
2	25	Rubberseed ..	OK	V. Sl. H. (D: 5 mins.)	Sl. H. (D: 45 mins.)	H (D: 24 mins.)	P. W.
	25	Linseed ..	OK	OK	V. Sl. H. (D: 20 mins.)	H (D: 80 mins.)	P. W.
3	35	Rubberseed ..	H (D : 3 hrs.)	V. H. (D : 8 hrs.)	W (D. N. D)	P. W. (D. N. D)	
	35	Linseed ..	OK	Sl. H. (D : 2 hrs.)	H (D : 24 hrs.)	P. W. (D N D)	

OK = Satisfactory, Sl. = Slight, D = time taken for haze to disappear, W = Whitness, H = hazy, V. Sl. = Very slight, D.N.D. = Does not disappear, P.W. = Pronounced whiteness, V.H. = very hazy.

been extended to rubberseed oil (iodine value 132). In this case it has been found possible to prepare tack-free oleo-resinous varnishes upto an "oil length" of 37½ gallons as against 18 gallons in the case of cotton-seed oil. (Oil length signifies gallons of oil per 100 lbs. of resin.) Any further increase in the proportion of the oil was found to result in tacky finishes. It was further observed that oil containing high proportion of free fatty acids can also be utilised, if the formulation includes a sufficient excess of glycerol for esterifying the free fatty acids.

Oleo-resinous varnishes of '15', '25' and '35' gallon oil length based on rubberseed oil were prepared and their properties compared with similar varnishes made from linseed oil. For the purpose of testing, all the varnishes were adjusted to viscosity E (Gardner-Holdt), then applied on carefully cleaned tin panels, and allowed to air-dry for seven days. The scratch resistance of the films was evaluated by determining the loads required for rupturing films on standard scratch test apparatus. The results are reported in Table 5.

The water-resistance of the air-dried films was evaluated by dipping the panels in water for periods of 1, 2, 4, 24 and 48 hours. The results are reported in Table 6.

Conclusions

From the foregoing experiments it may be concluded that heat treatment of the seeds does slow down the deterioration, though it does not completely prevent it. The oil extracted from white and cream varieties by solvent extraction has excellent keeping qualities. Rubberseed oil can be used as such for preparing tack-free finishes, which compare favourably with similar varnishes prepared from linseed oil.

Further studies with special reference to the polymerisation of the oil from heated kernels is in progress.

Acknowledgements

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UTILIZATION OF SOME RARE VARIETIES OF EAST PAKISTAN LIMES

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As a result of preliminary botanical and physical investigations,[1] the general properties of some of the citrus fruits found in East Pakistan have shown them to be similar to limes. However, they are not same as those already described in the literature.[2] The different varieties of the locally available limes were carefully chosen and subjected to analysis for their major constituents. One typical variety called "gandharaj" (king of odour) is shown in Fig. 1. It

Fig. 1.—Gandharaj ($\frac{1}{2}$ size).

was thoroughly analyzed and the different data was then compared with those of others in order to establish their significance in commerce. The identification and characterization of the constituents of gandharaj left no doubt about their value for human consumption.

Experimental

Materials.—These citrus fruits are grown all over Chittagong and Dacca sub-divisions, and were collected from Dacca markets and around. Three freshly distilled solvents, (1) alcohol over KOH + pinch of Na_2O_2, (2) ethyl ether over KOH, and (3) petroleum ether, 40-60°C., alone were used. The other chemicals were at least chemically pure.

Apparatus and Methods.—The total content of acid, sugar, pectin, vitamin C, iron, calcium and phosphorus have been estimated by the standard methods [1,3-5]. The quantity of essential oil in the peel was also determined.[6]

The pure pectin from gandharaj albedo was prepared by a modification of the existing procedures. The fresh albedo 700 g. was refluxed with 95% alcohol for 24 hours. The alcohol was then decanted off. The procedure was repeated four times, the residue filtered dry over a Buchner funnel and further refluxed with ethyl ether three times in succession. A portion of the solid samples (100 g.) was ground, suspended in 0.05 N HCl, using 20 ml. per g. of dry material and heated to 80°C. (critical) on water bath for 2 hours with occasional stirring. On cooling, the material was filtered through a linen cloth and the residue was treated another three times with such hot acid media in order to extract all pectinic acid substances (water-soluble pectin). This pectin solution was mixed with alcohol until 60% alcohol concentration was attained. After keeping for 12 hours (or overnight), the mixture was filtered through a silk cloth of fine mesh, washed free of acid with water-ethanol (1 : 2) and resuspended in 95% alcohol. The dry pectin was recovered by filtration and washing with 95% alcohol and ether in succession, and then subjected to different analyses : estimations of uronic acid,[8] calcium pectate[9] and methyl ester.[10]

A column of activated charcoal plus filter-paper pulp in place of filter aid (18.0×3.4 cm.) was used[11] to separate the sugars in the gandharaj aqueous extracts purified by basic lead acetate procedures.[12] All possible monosaccharides were tested in water eluates and disaccharides in the eluate of 5% ethanol solution. The organic acids in the total water extracts were neutralized by milk of lime (1.5%). The precepitated calcium salts were decomposed by 0.1 N sulphuric acid and the resulting mother liquor after decolorization with activated charcoal was analyzed for different acids according to the methods of Mollow Perkin.[13]

The preparation of beverages from essential oils ; of jams, jellies and marmalades from pectin and peels of gandharaj ; preservation of deaerated juice and 'gandharaj' hearts (unbroken juice cells) ; preparation of dried pomace and 'morabba' from albedo, and of citric and ascorbic acids from aqueous extracts were attempted through the standard procedures.[14]

Results and Discussion

Table I shows the distribution of major con-

stituents in gandharaj as compared with the other varieties of limes in East Pakistan. The different varieties are very similar in their composition. Furthermore gandharaj consists of substances almost identical with those of California lime (Table 2). Only the protein content being somewhat different. Table 3 records the distribution of valuable chemicals in the different segments of gandharaj. The percentages of uronic acid, calcium pectate and methyl ester, as 72%, 98% and 9.2% respectively, leave no doubt about the characteristic nature of pure fruit pectin in gandharaj that also possesses glucose and fructose as monosaccharides and sucrose as only disaccharide. The presence of citric, tartaric and malic acids has been established, but the presence of oxalic acid is doubtful.

The beverages, jams, jellies, marmalades and juices have been found to possess good flavours and have a long shelf life (over three months). The preserved hearts were also pleasant to taste. The pomace yielded pectin whenever needed. The production of citric acid was successful but

TABLE 1.—COMPARATIVE ANALYSIS OF DIFFERENT VARIETIES OF EAST PAKISTAN LIME (CALCULATED ON DRY WEIGHT BASIS).

Sample	Local name	Total weight of fruit g.	Moisture %	Sugar %	Acid %	Pectin %	Vitamin C mg. %
1	Lamba kagji ..	45.0	81.0	8.5	26.4	19.1	966.2
2	Goal kagji ..	38.5	81.0	8.5	25.9	22.2	695.0
3	Kalambia ..	162.5	76.0	10.8	32.7	8.8	633.0
4	Bara pati ..	273.0	76.0	16.0	29.0	13.8	713.0
5	Ghora ..	325.0	75.0	11.9	31.52	11.8	413.0
6	Godha ..	352.0	75.0	12.2	30.5	11.8	397.8
7	Bara alachi ..	135.0	76.0	13.0	30.0	17.4	5.8
8	Chota kagji ..	25.7	81.0	3.7	25.9	24.6	103.9
9	Ghandharaj ..	80.0	78.0	5.11	26.9	17.2	483.6

* Local designation of the varieties by physical shapes : lamba = long, goal = round, bara = large, chota = small, kagji = lime, ghandharaj = king of odour.

TABLE 3.—SUGAR, ACID, PECTIN, AND VITAMIN C CONTENT OF DIFFERENT PARTS OF GANDHARAJ (CALCULATED ON FRESH WEIGHT BASIS).

Different portions	Weight g.	Moisture average %	Total sugar %	Acid %	Pectin %	Vitamin C mg. %
Flavedo	15.5	75.0	2.3	0.3	3.6	16.6
Albedo	17.0	79.0	4.6	0.30	4.2	9.9
Pulp	47.5	88.0	1.4	4.90	3.8	168.0
Whole fruit	80.0	78.0	2.3	5.80	3.8	106.8

Table 2.—Comparative Analysis of Lime (Dry Weight Basis; Values per 100 g.).

	Lime (California)		Ghandharaj (E. Pakistan)	
	Dried peel	Juice	Dried peel	Juice
Protein	6.39	—	10.50	—
Crude fat	1.23	—	1.40	—
Crude fibre	15.00	—	15.40	—
Ash	5.04	—	5.25	—
Water	7.10	—	0	—
N-Free — extract	65.24	—	76.45	
Minerals Fe	—	—	0.02	
Minerals Ca	—	—	1.51	
Minerals P	—	—	0.17	
Total sugar	—	2.2-6.0	11.5	1.4
Acid	—	6.0-7.0	1.7	4.9
Vitamin C (mg.)	—	67.0	83.0	168.7
Essential oil	0.7 cc*	—	3.5 cc.	—

*Fresh weight basis.

that of ascorbic acid was only partially so. The albedo portions of the fruits produced luscious 'morabba' and candied materials, which were appreciated by a panel of tasters. Further work is in progress and will be published later.

Acknowledgement

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INVESTIGATIONS ON THE BY-PRODUCTS OF THE RICE MILLING INDUSTRY

Part I.—Minerals and Vitamins B and E in the Various Rice Fractions

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Introduction

The average annual total production of rice crop in Pakistan is placed at 8,320,000 tons out of which nearly 806,000 tons are produced in West Pakistan and approximately 7,514,000 tons in East Pakistan. In most areas of Sind, machine milling is in vogue, and during the whole process, five fractions, namely, polished rice, 'tuttar' (hulls), 'tutri' fine 'kutti' (polishings), and broken rice, are obtained in the following proportions :—

Fraction	Unparboiled Rice	Parboiled Rice
Polished rice ..	60—63%	70—75%
Tuttar (Hulls) ..	16—20%	16—20%
Tutri (Middlings) ..	1— 2%	2— 3%
Fine Kutti (Polishings)	6— 7%	2— 3%
Broken rice ..	2— 4%	Negligible

A considerable portion of the hulls are utilised as fuel in the parboiling and also for domestic cooking. Tutri and fine kutti are used chiefly as cattle feed, while broken rice is sold as such in the market for human consumption.

A much greater degree of refinement is achieved with machine milling as against hand pounding, although this increase is usually at the cost of some valuable nutrients, such as proteins, fats, minerals and some very important vitamins of the B-complex group especially thiamine. The incorporation of preliminary outmoded techniques, such as undermilling and parboiling has done much to retain the natural nutrients including B-complex vitamins of the whole grain, but, due to some disadvantages inherent in these processes, they have received only a limited acceptance. For example, the products obtained after parboiling are somewhat different from the ordinary white rice both in appearance and flavour, and are therefore less acceptable to the average consumer. A large proportion of the valuable minerals and vitamins, thus, continue to be lost in the third and the fourth fractions mentioned above. It was therefore, considered of importance to investigate the possibility of utilising these by-products of the rice milling industry as sources of vitamin 'E' B-complex vitamins, and other essential nutrients. Experiments in this connection have resulted in some very encouraging results and the preliminary findings obtained in the course of this study are presented in this paper.

Experimental

Materials and Methods.—Paddy and the other fractions were obtained through the courtesy of Mr. Mohammad Sami, proprietor of Wasi Mohammad Mohammad Sami Rice Milling Factory, Larkana (Sind).

Decalso 'Y', of the Permutit Company, London, was used as an ion exchange resin for the absorption of vitamin B_1 from the crude extract. It was activated by treating twice with hot 3% acetic acid, followed by 25% potassium chloride solution. After draining off the potassium chloride, the Decalso was once again washed with hot acetic acid, and finally with hot water till the final washed solution was free from chlorides. The activated Decalso was dried at room temperature and then used. The whole process of activation was carried out in a Buchner funnel.[1]

Weighed amounts of each fraction evenly powdered were then submitted to chemical analysis. Moisture, ash, silica, calcium and proteins were determined according to standard methods of analysis of the A.O.A.C.[2] Specific methods are described under the appropriate headings below. The results obtained for moisture, minerals, proteins and vitamin B_1 are given in Table 1, while those for the rice oil and vitamin 'E' are shown in Table 2.

Phosphorus.—Phosphorus was determined by the method of Berenblum and Chain.[3] This method is based on the ready solubility of the reducible phosphomolybdic acid in isobutyl alcohol. It consists in the reduction of phosphomolybdic acid to the blue complex by shaking the alcoholic extract with an acidified aqueous solution of stannous chloride. The intensity of the

blue colour produced was measured in a Hilger photoelectric colorimeter using filter 70 (Table 1).

Thiamine.—Thiamine was determined fluorometrically by the thiochrome method.[1] The process involves the extraction of the vitamin followed by dephosphorylation by heating first with 0.1 N hydrochloric acid in a boiling water bath and then incubating at 45°-50°C. with 6% solution of Taka Diastase (Parke Davis and Co., New York) in 2.5 M sodium acetate solution, after adjusting the *p*H to 4.5. The extracted vitamin was then purified by adsorption-elution on a column of Decalso and the fluorescent thiochrome produced after treatment with alkaline potassium ferricyanide was extracted with isobutyl alcohol, was measured on a photoflurometer.

Fat from Rice Fractions.—Each fraction was well powdered and its oil was extracted with ether in a Soxhlet apparatus. The ether extract was dried with anhydrous sodium sulphate and filtered in a tared flask. The solvent was distilled off, the last traces being removed in vacuo, and the oil was recovered and weighed (Table 2).

Determination of Vitamin 'E'.—Rice oil was first of all treated according to the method of Parker and McFarlane,[4] which consists in shaking the petroleum ether solution of the oil with 85% sulphuric acid. In this way quinones and other unsaturated substances were made water soluble and removed. Vitamin E was then determined colorimetrically by the ferric chloride—α-α′ dipyridyl method of Emmerie and Engel.[5] The red colour produced was measured in a Hilger photoelectric colorimeter using filter 52. A standard curve was prepared for different concentrations of the vitamin by using α-tocopherol (Merck). (Table 2).

Table 1.—Showing the Analysis of Unparboiled Paddy and its Fractions*.

	Moisture %	Ash %	Silica %	Calcium (CaO) %	Phosphorous (P_2O_5) %	Protein %	Nitrogen free extract † %	Fibre %	Vit. B_1 (thiamin) µg/gm
Paddy ..	12.30	6.62	2.80	0.13	0.62	6.03	62.75	10.20	3.3
Hulls ..	10.10	20.83	16.40	0.32	0.31	2.77	24.75	39.85	0.4
Tutri ..	11.05	22.64	13.50	0.21	—	3.78	—	—	2.5
Fine Kutti ..	8.76	14.30	9.1	0.38	2.68	12.84	33.37	20.05	14.0
Polished rice ..	13.06	0.90	0.11	0.05	0.45	6.62	78.32	3.40	0.6

* The percentage of fat in various fractions is given in Table 2.

† Calculated by difference.

Table 2.—Showing the Analysis of Oil from Unparboiled paddy and its Fractions.

	Oil %	Acidity as oleic acid %	Iodine value	Refractive index at 40°C.	Saponification value	Vitamin E mg./100 g.
Paddy	2.1	6.1	82.9	1.4680	186.6	110
Hulls	1.7	9.3	—	1.4635	—	—
Tutri	5.7	25.4	80.5	1.4630	185.4	140
Fine Kutti	10.68	28.7	82.2	1.4660	188.3	162

Higher values of vitamin E were, however, recorded if oil was not previously treated according to the method of Parker and McFarlane, and this treatment became particularly indispensible in the case of oil extracted from rice fractions stored for a year or more. The change in acidity of stored oil, noted by the authors has also been recorded by other workers.[6,7]

Discussion

From Table I it is clear that out of all the fractions obtained as by-products of the rice milling industry, fine kutti is the richest in vitamin B_1 and other nutrients. The hulls, as expected, are very rich in silica and this is responsible for their utilisation in the glass manufacturing industry in Italy. The hulls have also been used for the production of activated carbon, water proof boards and a host of other products.[8] Further, the use of the hull ash as an insulating agent (due to the cellular structure of the silica) holds considerable promise.[9] Values from 6 to 10% of mineral matter, and 13 to 30 ug/mg of thiamine [10] have been reported in the literature. The abnormally high proportion of ash and comparatively low vitamin B_1 content noted by present authors in fine kutti is probably due to the contamination of this fraction with the hulls during the hand sifting of the fraction.

Rice oil needs special consideration. Table 2 shows that 10 to 12% of the oil, containing 0.1-0.2% of vitamin E, could be easily extracted from fine kutti. Because of the presence of vitamin E, which acts as an antioxidant, this oil can be stored over long periods without developing rancidity. It has also been reported that after purification rice oil can become a nutritionally valuable and acceptable edible oil.[12]

A large increase in acidity was observed in the oil extracted from the stored rice fractions, the acidity shooting upto about 80% in six months. Other workers have also noticed such an increase in the acidity of the rice oil on storage,[11] and it is reported to be due to the splitting of the fat by the lipases.

Rice oil being a very potent source of vitamin E, can be exploited for the production of vitamin E concentrate, which can be usefully employed as an antioxidant in food technology. Further work in this direction is in progress.

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FUNGICIDAL PROPERTIES OF SHARIGOL

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Introduction

In an earlier communication, some preliminary results on the fungicidal activity of Sharigol against *Aspergillus niger* and *Alternaria sp.* have already been reported,[1] from which it appears that Sharigol shows promise of being a good fungicide. It was, therefore, considered important to extend this study to human pathogens and other important fungi. The present paper presents a study of the fungicidal effects of Sharigol against the human pathogens, *Aspergillus fumigatus*, *A. flavus*, *Trichopyton metalense*, and two other important fungi, *viz.*, *Helminthosporium oryzae* and *Empusa muscae*.

Effect of Sharigol on the three Human Pathogens

Preliminary tests were done by mixing the chemical with the medium in varying concentrations in the petri dishes, Sabraud's medium being used.

To facilitate a detailed examination of the effect of different concentrations of Sharigol on the growth and sporulation of the three pathogens, a series of experiments was conducted, using Sharigol concentrations from 1 : 1200 to 1 : 40 in 11 steps. In the first series of experiments, Sharigol was mixed in the ratios of 1 : 1200, 1 : 600, 1 : 400 with the medium, and a control was also kept with the series. The medium was then inoculated with a suspension of spores in sterile distilled water prepared by vigorously shaking about 8 ml. of water in a 7-day old culture tube and standardizing the suspension of spores thus obtained so that the number of spores per unit field under the microscope was constant. Three replicates were taken in each series of experiments and observations were made every 24 hours, the minimum and maximum growth for every concentration and every species were noted. The first four rows of Table 1 show the results for the control and the three different concentrations of Sharigol, while the rest of the table shows the data obtained with the higher concentrations.

After 24 hours some growth was observed in the control, but in 1 : 1200 concentration no growth was found. After 48 hours abundant growth was observed and sporulation had started in the control, whereas no growth was observed in the treated petri dishes. After 72 hours the mycelium had spread to a diameter of about 4 to 4.5 cms. in the control and sporulation was abundant, while in the treated petri dishes very small growth had taken place without any sporulation. The inhibitory effect of low concentrations of Sharigol on the mycelial growth and sporulation is thus evident. In the control, sporulation started between the second and third days, while in the petri dishes with Sharigol concentrations of 1 : 1200, 1 : 600 and 1 : 400 sporulation started between the 4th and 6th, 7th and 8th, and 9th and 10th days, respectively.

Inorder to study the effect of higher concentrations of Sharigol, further experiments on the above lines were conducted with concentrations upto 1 : 40, the results of which are also given in Table 1. They indicate that the inhibition of growth as well as the delay in sporulation is proportional to the increase in Sharigol concentration in the medium.

In the concentration of 1 : 80, no growth was observed upto 4 days and on the 5th day, in a few petri dishes (*Aspergillus fumigatus* and *A. flavus*) a minute dirty speck was observed, (Plate No. 1). The increase in size of these specks was extremely

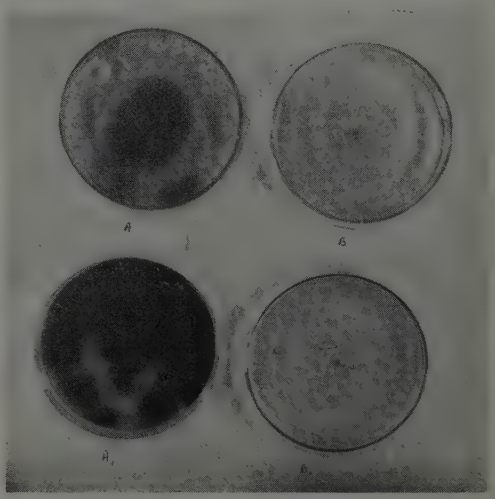


Plate No. 1.—Top - *Aspergillus flavus* A, control; B, 1:80 Sharigol (After 120 hours). Bottom: *Aspergillus fumigatus* A_1 control; B_1 1:80 Sharigol (After 120 hours).

slow. In the case of *Trichophyton metalense*, no growth was observed, and later on it was found that in the concentration of 1 : 60 sometimes the germination fails. In the concentration of 1 : 50 the germination of spores usually fails but sometimes very minute specks of growth may be found. In the concentration of 1 : 40, germination of spores fails and no growth is observed even after keeping the petri dishes for about two months. The time taken for sporulation in the concentrations of 1 : 80 and 1 : 60 is between 23 to 25 and 25 to 28 days respectively. In the concentration of 1 : 50 no sporulation takes place.

Some Abnormalities in Growth due to Sharigol

During the course of study of the effect of Sharigol on fungi some abnormalities in mycelial growth were noted. In concentrations of Sharigol, from 1 : 1200 upwards, the growths were elevated and cushion like, as already reported by Quraishi

TABLE 1.—CONCENTRATION GROWTH.

Sharigol concentration	Test specimen	1 day	2 days	3 days	4 days	5 days	6 days	7 days	Time taken for sporulation
Control	*A. fumigatus* ..	Speck	1.4-2.0	3-4.5	5-6	7-8.5	9-9.5	9.5-10	2-3 days.
	A. flavus ..	,,	2.0-3.0	3.5-4.5	5-5.5	6-6.5	7-8.5	8.5-9.5	
	T. metalense ..	,,	0.5-1.0	1.5-2 5	2.8-3.5	3.5-4.5	5-6	6.5-7.5	
1 : 1200	*A. fumigatus* ..	No	Speck	0.5-1.0	1.5-2	2-2.5	3-3.5	3.5-4,0	4-6 days.
	A. flavus ..	Growth	,,	0.2-0.5	0.8-1.2	1. 5-2	2. 5-3.0	3.5-4.5	
	T. metalense ..	,,	,,	0.2-0.3	0.5-0.8	1-1.8	2. 3-2.8	3.5-4.0	
1 : 600	*A. fumigatus* ..	,,	No	0.4-0.9	0.9-1.1	1. 3-1.5	1. 5-2	2.2-5	7-8 days.
	A. flavus ..		Growth	Speck-0.1	0.5-0.8	1. 0-1.5	1. 8-2	2.5-3.0	
	T. metalense ..		,,	Speck	0.2-0.5	0. 8-1.5	2-2.5	2.8-3.2	
1 : 400	*A. fumigatus* ..	,,	,,	,,	0.2-0.3	0. 4-0.6	0. 8-1	1.3-1.5	9-10 days.
	A. flavus ..	,,	,,	,,	0.1-0.2	0. 5-0.7	0. 8-1	1-1.7	
	T. metalense ..	,,	,,	,,	0.2-0.4	0. 6-1.2	1. 5-2	2.5-3.0	
1 : 300	*A. fumigatus* ..	,,	,,	,,	Speck	0. 2-0.4	0. 5-0.8	1-1.2	10-15 days.
	A. flavus ..	,,	,,	,,	Speck-0.1	0.25-0.35	0. 4-0.6	0.7-1.5	
	T. metalense ..	,,	,,	,,	0.2-0.3	0. 5-1.0	1. 2-1.5	2-2.5	
1 : 200	*A. fumigatus* ..	,,	,,	No Growth	Speck	0. 1-0.2	0.25-0.3	0.5-0.8	15-18 days
	A. flavus ..	,,	,,	Speck	,,	0. 2-0.3	0.35-0.4	0.5-0.9	
	T. metalense ..	,,	,,	No Growth	Speck-0.2	0. 4-0.6	0. 8-1.2	1.5-2.5	
1 : 150	*A. fumigatus* ..	,,	,,	,,	Speck	Speck-0.1	0. 2-0.25	0.3-0.35	18-20 days.
	A. flavus ..	,,	,,	,,	,,	Speck-0.2	0. 3-0.4	0.4-0.8	
	T. metalense ..	,,	,,	,,	Speck-0.2	0. 2-0.4	0. 5-1	1.2-2.0	
1 : 100	*A. fumigatus* ..	,,	,,	,,	No	Speck	0. 1-0.2	0.2-0.3	20-22 days
	A. flavus ..	,,	,,	,,	Growth	,,	0.15-0.3	0.3-0.5	
	T. metalense ..	,,	,,	,,	,,	,,	0. 1-0.2	0.5-0.8	
1 : 80	*A. fumigatus* ..	,,	,,	,,	,,	,,	Speck-0.1	0.15-0.2	23-25 days.
	A. flavus ..					,,	0. 1-0.25	0.15-0.2	
	T. metalense ..					No Growth	Speck-0.1	0.2-0.3	
1 : 60	*A. fumigatus* ..	,,	,,	,,	,,	,,	Speck	Speck-0.2	Slight sporulation only in some cases 25-28 days.
	A. flavus ..	,,	,,	,,	,,	,,	,,	Speck-0.1	
	T. metalense ..	,,	,,	,,	,,	,,	No Growth	0. 1-0.2	
1 : 50	*A. fumigatus* ..	,,	,,	,,	,,	,,	,,	Speck	No Sporulation found after 60 days.
	A. flavus ..	,,	,,	,,	,,	,,	,,	,,	
	T. metalense ..	,,	,,	,,	,,	,,	,,	Speck-0.1	
1 : 40	*A. fumigatus* ..	,,	,,	,,	,,	,,	,,	No Growth	No Growth and no sporulation after 60 days.
	A. flavus ..	,,	,,	,,	,,	,,	,,	,,	
	T. metalense ..	,,	,,	,,	,,	,,	,,	,,	

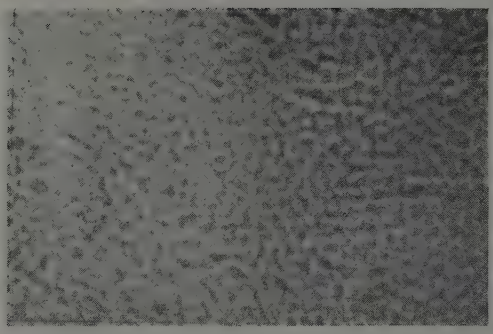


Plate No. 2.—Meshed mycelium of *Aspergillus* Sp. in 1:600 Sharigol.

and Hussain.[1] The contour of the growth was usually irregular and the colour was muddy. The growth of the mycelium was compact and meshed, (Plate No. 2). In the higher concentrations two regions were observed in the cushion-shaped growth, the mycelium being very compact and meshed in the outer region of the cushion forming a pseudoparenchymatous structure, but underneath it the mycelium was loose and individual filaments could be seen under the microscope. Changes in the cell dimensions of the mycelium were also noted and will be reported upon later.

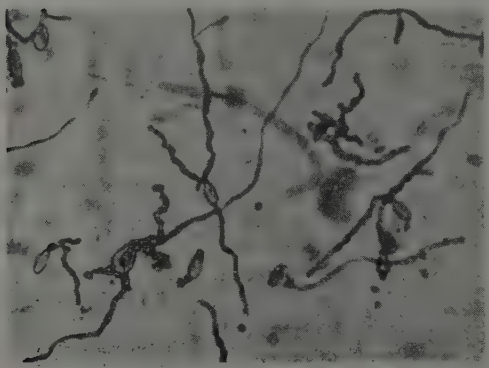
Effect of Concentration on Spore Germination in Helminthosponium oryzae and Empusa muscae

Spores of *Helminthosporium oryzae*, *Aspergillus flavus* and *Empusa muscae* were taken for germination study, which was carried out by the simple method of M. Checogne and Viel[2] on microscope slides ringed with paraffin wax. A suspension of spores was prepared by the method previously mentioned, and was filtered through a pad of sterilized glass wool to remove the pieces of mycelium from the culture. The suspension was standardised as before to obtain a definite number of spores per unit field. Sharigol and a solution of glucose were mixed with portions of the suspension in such a way that the mixture contained 5% of glucose with the following concentrations of Sharigol :

0.01%, 0.02%, 0.03%, 0.06%, 0.09%, 0.18%, 0.25%, 1.0%. Teepol (sodium secondary alkyl (C_{10}-H_{18}) sulphate) was used as an emulsifying agent.

Two drops of each of the above suspensions were dropped inside respective wax rings on glass slides, which were then placed on glass strips and kept in large petri dishes, (Plate No. 3). A slide

Plate No. 3.—Spore germination on the wax-ringed slides placed on glass strips.



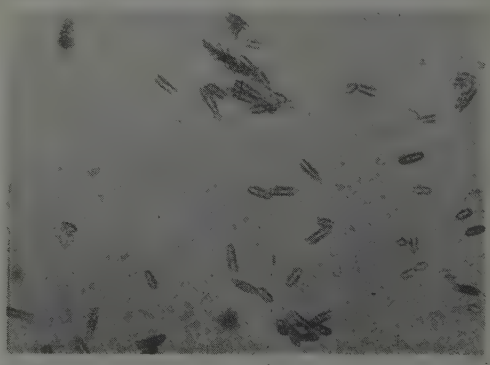


Plate No. 4.—Spores of *Helminthosporium oryzae* after 24 hours incubation at 25-27 °C. (a) without Sharigol, showing germinating spores (b) with 1.5% Sharigol, showing non-germination of spores.

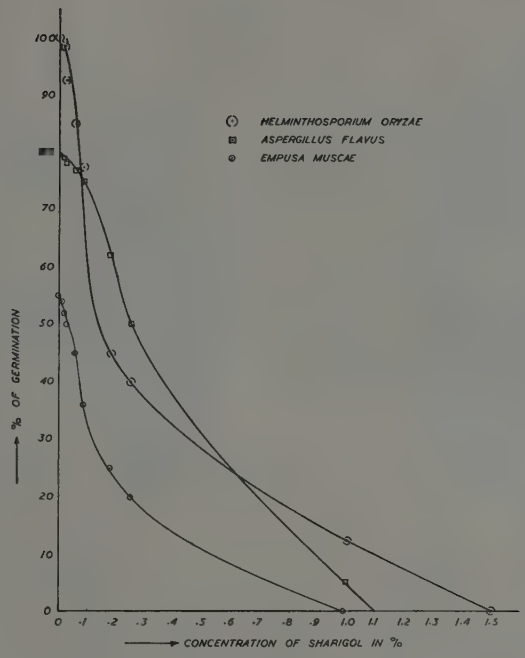


Fig. 1.

without Sharigol was kept as control. To maintain proper humidity, 10 ml. of 20% solution of glycerol were poured into each petri dish and the petri dishes were kept in an air-conditioned room (25°C.-27°C.) for 24 hours. Two replicates were done in each series of experiments and several series of experiments were conducted.

All the slides were studied under the microscope after 24 hours and the percentage of germination was noted (Plate No. 4). These percentages were plotted on the graph against the appropriate concentrations, and three curves, for the three species used, were obtained (cf. Fig. 1).

The graphs show that the percentage of germination decreases regularly with the increase of concentration of Sharigol and at a certain limiting concentration the spores fail to germinate. In the case of *Helminthosporium oryzae* this limiting concentration is 1.5%, in *Aspergillus flavus* 1.1%, and in *Empusa muscae* 1.0%.

Conclusions

Whereas for fungi of agricultural importance, as reported previously by Quraishi and Hussain, small concentrations of Sharigol are enough to check the growth and sporulation, it appears from the above experiments that considerably higher (*about ten times*) concentrations of Sharigol are needed to check the growth of fungi pathogenic to human beings. These results agree with observations previously made on the resistance of fungi pathogenic to man. It may be pointed out here that a certain amount of variation in these experiments is to be expected because the coal supplies from which Sharigol has been obtained tend to differ to some extent, thereby causing some differences in the composition of Sharigol obtained in different batches.

Acknowledgement

The authors acknowledge with thanks the help and valuable suggestions they received from Dr. Salimuzzaman Siddiqui. The authors also wish to thank Dr. A.A. Anwar, Head of the Microbiology Department, Karachi University, for supplying the cultures of fungi pathogenic to man.

References

1. M.S. Quraishi and S.S. Hussain, Pakistan J. Sci. Ind. Research, **1**, 93 (1958).
2. M. Chacogne and G. Viel, Annales des epiphyties, **4**, 641-660 (1956).

BERGINUS MAINDRONI AND OTHER BEETLES IN STORED LAC

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For over three years experiments have been in progress, using Sind brood lac for experimental cultivation and for the study of the associated parasites. About 2 lbs. of brood lac, *i.e.*, fresh stick lac, was received twice a year from Khattar Forest Range, Hyderabad Sind, where *Lakshadia sindica* is regularly cultivated on *Acacia arabica*. Among the beetles was found *Berginus maindroni* belonging to *Lyctidae*, previously classed among the *Colydiidae*. In the course of studies on various lacs it was found to be universally distributed, perhaps the one beetle, not absent from any lac including those of Tonkin, Burma, Assam, India and Pakistan. Fig. 1 shows its appearance as seen from above. Its pupa was also studied, and Fig. 2 gives its ventral view, Fig. 3 its dorsal appearance, and Fig. 4 shows it sideways.

Its larva is a delicate roundish creature, which has not been illustrated so far. No proper study has hitherto been carried out to establish if this beetle larva is injurious to the living lac insect. The present study shows it to be a scavanger, feeding on half dead or dead lac insects.

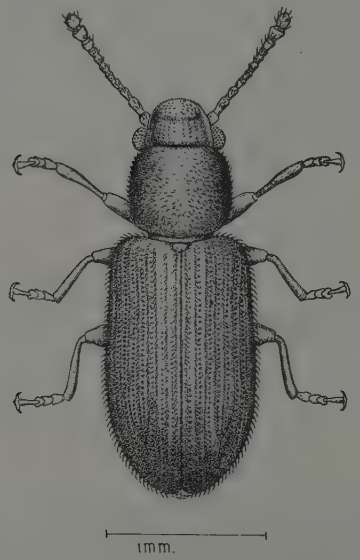

Fig. 1.—*Berginus maindroni*, adult bettle.

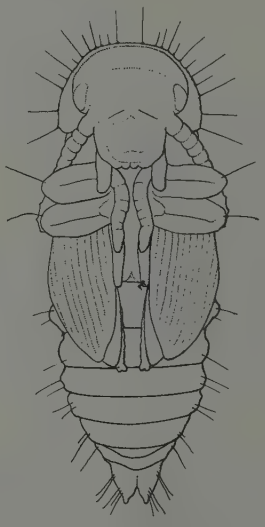

Fig. 2.—*B. maindroni*, pupa, ventral view.

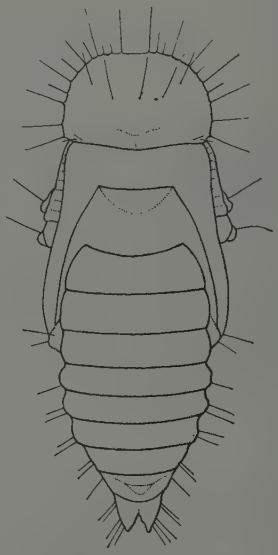

Fig. 3.—*B. maindroni*, pupa, dorsal view.

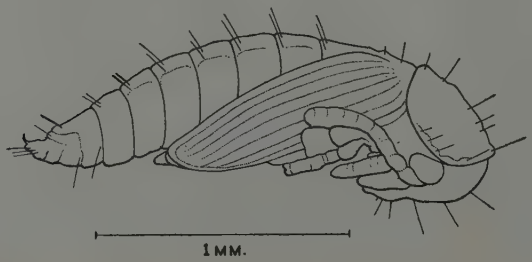

Fig. 4.—*B. maindroni*, pupa side view.

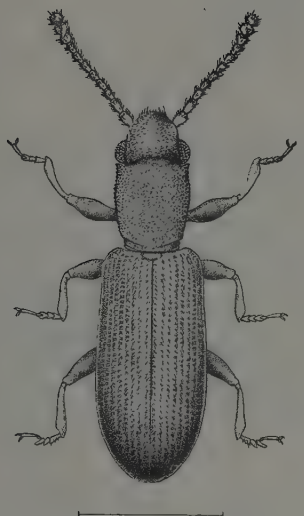

Fig. 5.—*Cathartus adrena*, adult beetle.

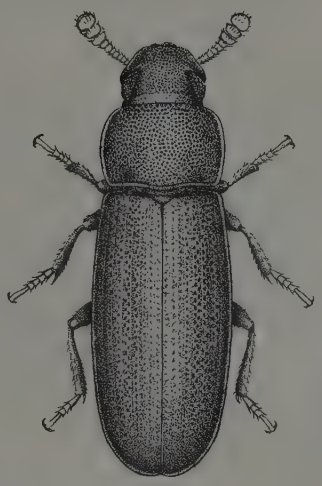

Fig. 6.—*Tribolium ferrugineum*, adult beetle.

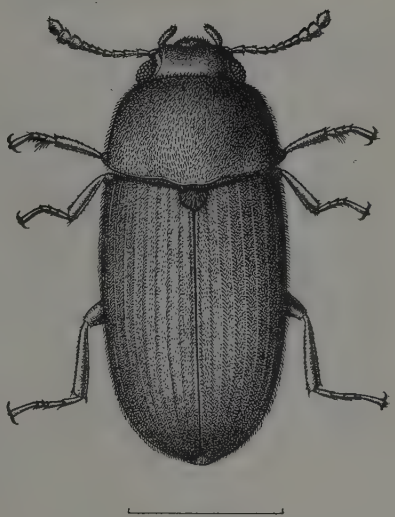

Fig. 7.—*Typhaea fumata*, adult beetle.

A similar beetle is *Cathartus adrena*, which is illustrated in Fig. 5. It has not yet been discovered in Sind lac, but the available record refers to very insufficient material, and since *Cathartus adrena* has been met with in most centres of lac cultivation in India, particularly from Mysore, it is very probable that Sind lac is also associated with it. Its pupa or larva has not been observed by any worker on lac, mainly because of the insignificant role it plays in the economy of lac cultivation.

When stick lac is stored, which means placed in heaps, a Tenebrionid beetle, *Tribolium ferrugineum*, Fig. 6, is found in great numbers. It is a saprophyte with a wide distribution, having been observed by the author even in Coca when a tin was left long unused. It is sure to be found with Sind lac when the stage comes of its being stored in some quantity. All these beetles have been recorded in other lacs by Imms and Chatterjee[1] before.

A much larger and active beetle, with its round worm-like larva even more active, is *Typhaea fumata*, of the family *Myctophagidae*, whose presence has not been reported by any other worker on lac. In Mysore, the author found it in such conspicuous numbers that he could not explain the absence of previous records, except on the basis that no special study had been devoted to the beetle pests of stored stick-lac. Its larva and pupae have been studied by the author. The insect is a universal saprophyte, being found even in old cigars, and, as such, is quite likely to appear in Sind lac on storage, and should be looked for in heaped lac.

Reference

1. A.D. Imms, and N.C. Chatterjee (1915) : *Biology of Tachardia lacca*. Ind. For. Mem. Vol. 3, Pt. 1.

DEVELOPMENT OF INLAND FISHERIES IN PAKISTAN

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Introduction

The development of fisheries in Pakistan presents different problems according to the particular part of the country for which a scheme of development is laid out, and no generalisation applicable to all places can be made. In this short note are presented the broad principles which should be kept in view before inaugurating any programme for the development of fisheries in Pakistan, with emphasis on the inland type.

The development of fishery falls under the following heads : (a) inland fishery with emphasis on the culture and preservation of fishes of economic value ; and (b) coastal fishery.

Closely connected with these are the important problems of (1) marketing of fish ; (2) transport ; (3) fish products including fish oils, guano and others.

Since inland fisheries stand most in need of development, we shall consider these here.

Inland Fisheries

There are two important principles which should be borne in mind if a good crop of fish is expected. The first is that a pond, like any agricultural land cannot be expected to yield an indefinite supply of crop unless it is treated with proper fertilizers and secondly, careful attention must be paid to "cropping" if fishes of good size are to be obtained. If the fish population is allowed to grow excessively, no fish will have a chance of attaining a good size, because roughly speaking a pond capable of supporting 100 lbs. of fish may either contain 100 fish weighing 1 lb. each or 400 fish weighing ¼ lb. each.

Although it is generally believed that fishery development is possible only in provinces having a large number of perennial tanks, nevertheless, seasonal tanks (which dry up either entirely or to a large extent during the summer) can be made to yield a good crop of fish if the following suggestions are adopted :

1. Large fingerlings about 6 months old should be stocked.

2. Before the tank dries up all fish must be removed, the large specimens being sent to the market and small ones kept for the second season.

3. The surface layer of the tank bottom should be lightly manured. These seasonal tanks can be worked very economically, because in large perennial ponds it is far more difficult to control the number, ages, and types of the different fishes and consequently it is difficult to gather a rich crop of economic varieties.

Basic Requirements

To ensure a regular supply of fresh water fish at a moderate price the following general measures should be adopted :—

(*a*) Establishment of stocking tanks.
(*b*) Control of destructive methods for catching fishes.
(*c*) Control of the size of the mesh.
(*d*) Construction of suitable hatchery centres for distribution of fry on a co-operative basis.
(*e*) Arrangement for rapid and safe transport of fish from one part of the country to the other.

The following fishes are suitable for stocking : *Labeo rohita* (local name : rohu, rohee (Bengal)) ; *Barbus* (Tor) *puititora* (local name : mahaseer) ; *Cirrhina mrigala* (local name : narain or naini) ; *Labeo calbasu* (local name : calbose) ; *Catla Catla* (Day) (local name : catla) ; and *Hilsa ilishia* (local name : hi'sa).

The above fishes are easily grown in tanks except hilsa, for which records are not available. Hilsa ascends up the rivers and is caught in very large numbers in Bengal and Sind, its flesh though spiny being very tasty and nutritious, so that in surplus areas a canning industry for this fish may be very profitable.

Suitable places for stocking are : (a) tanks ; (b) back-waters of canals and (c) large reservoirs. In tank stocking the following three factors should be kept in view : (1) nature of the tank ; (2) type of fish to be stocked ; and (3) supervision of the tank. These three factors are of vital importance because each of the operations is intimately linked with the other.

Types of Tanks

These are of two kinds :—

(a) *Seasonal tanks*.—These tanks start drying up in March and the entire crop must be taken out before they actually dry up. In June, they should be made ready for the next season by slightly manuring the surface, the manure consisting of decaying organic matter and lime. If new small tanks are laid for fry culture, they should have vertical sides and should not be more than 4 or 5 feet in depth. After four months the fry should be transferred to larger tanks for stocking. It is noteworthy that in East Pakistan fish cultivation has lately been started in paddy-fields with very encouraging results, and such paddy-cum-fish-culture should be easy to develop in similar regions of Assam.

(b) *Perennial tanks*.—These tanks are deep and contain water all the year round. They may be sub-divided into closed and open types, the latter being either temporarily or permanently connected with a river.

Closed tanks are just like agricultural fields which have to be manured and sown every year. They are good for stocking purposes and fry can be easily transferred into these and allowed to grow. Occasionally fish fauna of these tanks should de examined and predacious fishes should be netted out as far as possible.

Open tanks are connected with rivers and therefore offer a good breeding place for carps, which breed only in running water. During the monsoon, when connection is established between the tanks and a river, fishes of all sizes rush towards the tank and along with those come the brooders. Efforts should de made to divert the brooders to a side tank by erecting a mesh-barrier at the mouth of the main tank, the size of the mesh being 1 inch square. The fry when about 1 ″ long should be diverted to another shallow reservoir where it should be allowed to grow for 4 months and, after sorting, should be finally transferred to stocking tanks.

Methods of Increasing the Productivity of Pond Fishery

The crop of fish which can be produced from a pond can be increased either by supplying artificial food or increasing the natural food. Soya-bean, barley, and maize are good food for carps, while trout demands a fairly large proportion of animal food. The natural food supply can be appreciably increased by introducing chemical fertilisers and with proper application an increase of 100% in the yield is possible. A very important point is that, in lime-deficient soil, it is useless to add any chemical fertilisers until the requisite amount of this substance has been added. When this has been done, a dressing of organic or inorganic manure may be given to the tank bottom, the best inorganic manure being phosphate, to which the addition of calcium has been found to be profitable. In perennial tanks, manure should be spread as evenly as possible over the surface of water from a boat taking care to avoid local concentration.

The success of pisciculture depends to a large extent on the elimination of predacious forms like *Clarius*, *Macrones*, *Wallagonia*, *Ophiocephalus*, *Notopterus etc*. from tanks which have been stocked with carps. From the previous list of fishes suitable for stocking, it will be seen that the most suitable fish is the carp, but it should not be concluded that these are the only types that can grow in tanks. Shallow tanks with muddy water, which are unsuitable for carp-culture, should be stocked with the following fishes which can combat unfair weather more successfully than the carp because they are provided with air breathing apparatus : *Ophicephalus striatus*, (local names : murral, shol, Bengali lakhu marathi) ; *Anabas testudineus*, (local name : Kobhais Hindi, Coi Bengali Undee-Colhere, Malayelam) ; *Wallago attu*, (local names : Parhin Hindustani, Boyari Bihari, Shivada Marahathi) ; *Clarias batrachus*, (local names : Magur Bengali, Mangri Bihari).

Suitable tanks about 3 to 4 feet deep should be selected to introduce fry. The bottom should be well manured to produce plankton fauna which is a suitable diet for young fry. Artificial food like soya-bean, cereals, and slaughter house refuse can be given as an additional food. Tanks should be occassionally examined and all filth from the bottom should be removed as excess of carbon dioxide which is freely generated in the presence of filth, is injurious to fish.

NON-TECHNICAL NOTES

REFINING OF BALUCHISTAN SULPHUR ORE

Important reserves of native sulphur in Pakistan occur at Koh-i-Sultan. The Geological Survey of British India proved them to be feasible for exploitation in 1940. Out of a reserve of 1,50,000 tons of the ore, 66,300 tons were excavated till 1945, at a cost of about Rs. 30 lakhs. Due to unfavourable geographical and climatic conditions, a good amount of money had to be spent on means of transport of the ore. The main loading camp was at Batal. Later, a 2-mile roapway was installed between Miri deposits and Batal loading camp, at a cost of about Rs. 4 lakhs. This was disposed of at a nominal price just before the Independence and was removed to India.

At present, the place is in the same condition as it was before the war-time operations. All the roads have been washed away by the nullas. Nothing is left of the buildings except a few ruins. Even the road between Nokundi and the foothills of Koh-i-Sultan has been damaged.

About 15,000 tons of the crude sulphur ore belonging to two private concerns are still lying at Nokundi railway station ; 85,000 tons of the ore averaging about 50% sulphur is available for excavation and subsequent refining. This figure may be low, as further reserves may be available underneath or elsewhere.

It is difficult to give a correct idea of the cost of excavation of the ore. The original scheme submitted by Mr. E.R. Gree in 1941, anticipated an expenditure of Rs. 5,22,335 for quarrying 25,000 tons good quality ore (15,000 tons from Batal, 10,000 tons from Miri) and delivering it into railway wagons at Nokundi within six months. This included capital cost of Rs. 41,780 out of which Rs. 12,960 could be recovered on the completion of the operation. Average cost per ton of ore, delivered into railway wagons at Nokundi was estimated at Rs. 19/2 and Rs. 22/5 for Batal and Miri, respectively.

In view of the fact that the cost of living and consequently the cost of labour as well as the capital cost have increased considerably as compared with 1941, the excavation of the ore today would naturally cost more.

The sulphur is present in the crude ore in association with fine amorphous silica and sometimes with gypsum and alum. Methods tried to refine this ore include Calcarroni, steam liquation, froth floatation, zinc chloride method, etc. None of these could prove economically feasible so far, on account of one or more of the following reasons :

1. Fineness and amorphous state of the associated gangue material.
2. Unsatisfactory recovery of sulphur.
3. High cost of operation.
4. Specialized technique and equipment for operation.

To give an idea about the high capital cost, the most recent Chemicoprocess of America which comprises steam liquation and froth floatation, involves for a 10–ton plant, a cost of about $ 7,00,000 in America. It is roughly estimated that the cost of refining would be more than Rs. 250 per ton.

Soon after the Independence the importance of sulphur to the country as a stragetic raw material was realized. Some practical efforts were made to solve this problem. These efforts got an impetus by the sudden announcement of American sulphur suppliers to restrict the export because of their dwindling reserves. Consequently work carried out under a scheme sponsored by the Central Government in December 1950, and later continued under the P.C.S.I.R., has resulted in the development of a simple method for the refining of sulphur. A special feature of this process is that it does not require any specialized equipment or technique.

The total capital investment for a unit producing 1,500 ton per annum is about Rs. 2,00,000. The average cost of the finished product (sulphur) is about Rs. 223/8/- per ton.

Process

The process essentially consists of grinding the ore to a certain mesh size and heating it with a cheap chemical at 120-130 °C. for a short time. Sulphur melts to form globules. The coalescence is facilitated by the addition of a small quantity of a surface active agent. The colour of the globules indicates when the process is complete.

The mass is then quenched and solidified sulphur globules together with the gangue are allowed to fall in a column of water in a specially designed separator, whereby the globules get separated from the gangue in settling tanks and can be used over and over again. The sulphur recovered is more than 99% pure. The recovery is about 90-95%.

The equipment required consists of the following : jaw crusher, ball mill, electric motors, galvanised iron sheet tanks, melting pans, separators, furnaces, sieves and driers, settling tanks, and generators.

The process is covered by Pakistan Patents 107149 and 108018

Pre-Construction Cost Estimation

(Production Capacity = 1,500 tons per year)

Capital expenditure :	Rs.	
Equipment ..	72,000	
Building ..	30,000	
	10,200	
Running expenditure :		
Raw Materials ..	1,97,375	
Direct Labour ..	45,000	
Power ..	30,000	
Contingencies ..	2,000	
Depreciation @ 15% ..	15,300	
		2,98,675
Direct expenses :		
Establishment ...	22,875	
Promotion of the project at ½ % on Rs. 1,80,000/- (running expenditure for 3 months plus capital expenditure) ..	4,500	
		27,375
Interest on capital @ 6% on Rs.1,80,000		10,800
Insurance @ 2½ % on Rs.2,99,375 ..		7,485
Cost of production of 1500 tons of sulphur		3,35,335

Average cost Rs. 223/8/- per ton.

JUTOID WATERPROOF MATTING

Water-proofing of roofs is a necessity in a great many cases where light concrete, thatched roofings or damp-proof courses are used. Uptil now these demands have been met by importing certain products, which are a drain on the foreign exchange and are too high priced to be directly available to the masses or for the rehabilitation of displaced persons. A process has been evolved at the Central Laboratories of the Pakistan Council of Scientific and Industrial Research for the production of a cheap water-proof matting of jute fabric base and other indigenous raw materials with the help of simple equipment which can be locally fabricated.

This material has been tested to withstand the severity of temperatures of the order of 170°F. without any bleeding and has also been subjected to water-jet quenching for determining thawing effects. Besides, it has been exposed to local climatic conditions for considerable periods without appreciable deterioration.

The total estimated capital investment for a plant with an annual production capacity of 6,00,000 sq. ft. Jutoid matting is Rs. 1,29,291. The cost of production of the matting works out to 3 ½ annas per sq. ft. The prevailing prices for the material used for similar purposes fluctuate between 12 annas to a rupee per sq. ft.

Pre-Construction Cost Estimation

Capital expenditure		Rs.
Equipment		9,900
Building		7,000
		16,900
Direct expenses :		Rs.
Raw Materials		97,500
Direct Wages		9,900
Power		1,000
Contingencies		1,000
Depreciation at 10% on capital ..		1,690
Indirect expenses :		
Establishment		9,720
Promotion of the project at 2½% on Rs. 50,000		1,250
Selling expenses		4,200
Insurance at 2½% on Rs. 41,275 ..		1,031
		1,29,291

Total cost of producing 6,00,000 sq. ft. of Jutoid comes to Rs. 1,29,291.

Cost of production per sq. ft. 3 ½ annas.

AIR ENTRAINING AGENT FOR THE PRODUCTION OF FOAM CONCRETE

Air entraining agents are employed for the production of light-weight concrete, used in factories for thermal insulation or where lightness is demanded irrespective of cost.

While there is a very substantial demand for light-weight concrete as a constructional material, particularly in factories, its use in the country is limited on account of the non-availability of air-entraining agents locally.

As a result of the work carried out in the Central Laboratories, a process has been developed for the production of an air-entraining agent from hair and other proteinous waste materials.

The total capital invetsment in a unit of production with a capacity of 125 gal. per day to give 2000 cu. ft. of light weight concrete is estimated to be about Rs. 17,000 with an average cost of Rs. 4/4/- per gal. of the air-entraining agent.

The process consists of the following unit operations: cooking under pressure and filtering.

Equipment and Raw Materials

Pressure cooker (150-litre capacity), plate and frame filter press with hand pump, tanks (200-litre capacity), and kettle (100-litre capacity).

Pre-Construction Cost Estimation

(Production capacity: 37,500 gal. per annum or 125 gal. per day)

		Rs.	Rs.
Capital expenditure			
Equipment	..	12,000	
Building	..	16,000	
			28,000
Direct expenses per annum			
Raw materials	..	87,228	
Direct wages	..	7,920	
Containers	..	37,500	
Power	..	4,000	
Contingencies	..	5,000	
Depreciation @ 10%		2,800	
			1,44,448
Indirect expenses			
Establishment		6,120	
Promotion of the project @ 2½% on Rs. 67,000 (capital expenditure plus running expenditure for 3 months)		1,675	
			7,795
Selling expenditure	.. ..		1,800
Interest on capital @ 4% on Rs. 67,000			2,680
Insurance @ 2 ½ % on Rs. 1,15,228	..		2,880
Cost of production of 37,500 gals. per annum of air-entraining agents			1,59,603

Average cost-Rs. 4/4 per gal.

PRINTING AND OTHER OIL-BASED INKS

Printing and other oil-based inks are mainly composed of a pigment material and a vehicle, usually a drying oil, in which the pigment is distributed in a finely divided state. But to prepare a stable composition of the proper consistency, adhesion, flow, colour and brilliancy involves a specialised technique and rigid control of the process and formulation. The introduction of automatic printing machine demands still greater perfection and uniformity in ink composition. The manufacture of ink is, therefore, a highly developed art, but on account of its large and universal demand, good quality printing and other inks are produced in almost all advanced countries. Pakistan, however, does not have a well established ink manufacturing industry, with the result that almost all types of printing and other inks required in the country are being imported. Investigations were, therefore, taken up in the Central Laboratories of the Council of Scientific and Industrial Research on various types of oil-based inks, such as stamp cancelling, duplicating and news inks. As a result of these investigations it has deen possible to evolve various compositions for these inks, which dry mainly by absorption. They are almost exclusively based on indigenous raw materials and compare favourably with the best quality imported inks of each of these categories.

The estimated demand of the various kinds of inks based on the figures of import is as given below :—

1. Postal ink	..	10,000 lbs.	approx.
2. Duplicating ink	..	50,000 ,,	,,
3. News printing ink	..	100,000 ,,	,,

A unit with a production capacity of the above indicated quantities of inks is estimated to require the total capital investment of about Rs. 2,00,000.

The average cost of the ink in a unit of this size would be about Rs. 1/2 per lb. inclusive of overhead expenses, as compared to the prevailing market price of these inks indicated below :—

1. Postal ink .. Rs. 4/-/- to 5/-/- per lb.
2. Duplicating ink .. Rs. 9/-/- to 10/-/- per lb.
3. News ink .. Rs. 4/-/- to 8/-/- per lb.

Process and Equipment

The process consists essentially of preparing a stabilising varnish which is thoroughly mixed with other ingredients, the whole mass being then passed through a roller mill.

The equipment required is : edge runner, mixer, single and triple roll mills, straining and sieving machine, filling machines, and storage tanks, pumps, electric motors, laboratory testing equipment, etc.

All of these have to be imported from abroad.

Raw Materials

The raw materials involved are : rosin, oil (vegetable and mineral oils), pigment and chemicals.

All the raw materials are available in the country, except carbon-black, which represents only about 6.5% of the total value.

Pre-Construction Cost Estimation

Production Capacity

News ink	1,00,000 lbs./annum
Duplicating ink	50,000 lbs./annum
Stamp cancelling ink	10,000 lbs./annum

	Rs.	Rs.
Capital expenditure		
Equipment	1,17,000	
Building	41,200	
		1,58,200
	Say ..	Rs. 1,60,000
Direct expenses per annum		
Raw materials	59,000	
Direct wages	14,220	
Containers	40,000	
Power	3,000	
Contingencies	5,000	
Depreciation @ 10%	16,000	
		1,37,220
Indirect expenses		
Establishment	21,900	
Promotion of the project @ 2½% on Rs. 2,00,000 (Capital expenditure plus running expenditure for 3 months)	5,000	
		26,900
Selling expenses		4,200
Interest on capital @ 4% on Rs. 2 lacs		8,000
Insurance @ 2½% on Rs. 2,19,000		5,475
Total cost of production of 1,60,000 lbs. of inks		1,81,795

NOTES & NEWS

Commonwealth Conference on Patents

A conference on patents was held at Canberra from the 9th to the 22nd November 1955 and was attended by official delegations from Australia, Canada, Federation of Rhodesia and Nyasaland, Great Britain, India, New Zealand, Pakistan and South Africa. Observers from the International Union for the Protection of Industrial Property; the Chartered Institute of Patent Agents; the Australian and British Groups of International Association for the Protection of Industrial Property; the Trade Marks, Patents and Designs Federation; the International Law Association; the Institute of Patent Attorneys of Australia; and the Australian Associated Chambers of Manufacturers and of Commerce also participated in the Conference.

The Conference was formally opened by Senator J. A. Spicer, Q.C., Attorney General of the Commonwealth. It unanimously elected Mr. H. R. Wilmot (Commissioner of Patents, Australia) as Chairman, and Mr. J. L. Girling (Comptroller-General of Patents, Designs and Trade Marks, United Kingdom) as Deputy Chairman.

Review of Patents Procedure and Practices

While considering the first item of the agenda relating to a review of actual or anticipated developments and divergencies in patents procedure and practices within the Commonwealth in the period since the 1922 Conference, Mr. J.L. Girling (United Kingdom) suggested the compilation of comparative tables that would relate the laws of all Commonwealth countries to a standard law. He submitted that the British law as brought up to date by the 1949 Patents Act and Rules was appropriate for consideration as the standard law. He emphasized that the object of his suggestion was that when Commonwealth countries legislated they should have in mind what other Commonwealth countries had done and so avoid deviation from their laws through ignorance. He then moved a resolution recommending each member country of the Commonwealth to prepare a comparative statement of its statutory law taking the United Kingdom Patents Act and Rules of 1949 as the yard-stick of comparison. The resolution was carried unanimously.

Problems Associated with Searching

Mr. J.W.T. Michel (Commissioner of Patents, Canada) introduced the discussion on the item relating to problems associated with searching and explained that under the Canadian Patents Act the Patent Office could request the submission by the applicant of a list of citations from any country. Dr. J. W. Miles (sometime Deputy Commissioner of Patents, New Zealand) said that there was substantially similar provision under the New Zealand statute. Mr. Wilmot (Australia) enquired whether some arrangement could be provided whereby offices could communicate the result of their searches to other offices. He asked whether the Conference agreed that offices should or could supply information about citations before acceptance in the originating country. Mr. Girling said this would involve some breach of confidentiality and an amendment of the British Act in this respect would be necessay, and this might well be controversial.

Dr. Miles (New Zealand) queried whether an applicant had any such right of secrecy. He suggested that patent offices must come into line with industrial organisations in the interchange of information and drew a comparison with associated companies in various countries that work as single units in the administration of their business. Mr. Girling remarked that the onus of supplying information should remain on the applicant. Messrs. Triggs, Hack and Stanfield (observers) referred to practical difficulties involved in communication by offices of the results of searches and favoured the New Zealand or Canadian systems.

Mr. H. Davies (Deputy Commissioner of Patents, Australia), after accepting an amendment by Mr. Girling, then moved the following resolution which was carried unanimously: "That the countries of the British Commonwealth that undertake a novelty search consider bringing down legislation to request applicants to supply the result of searches."

Problems Associateed with Classification

Mr. Wilmot (Australia), in introducing the discussions on problems associated with classification, considered that two matters were involved:

(1) problems arising from any system of classification, and (2) problems relating to the development of a particular type of classification. Mr. Girling (United Kingdom) thought that it might be preferable to discuss first the possible adoption of an intra-Commonwealth classification. This was agreed to and a general discussion then followed, in which each delegate described the classification system in his own country.

Mr. Girling described the problems that the Council of Europe classification attempted to solve, and pointed out that an additional objective of the scheme was that the countries of the world might endeavour, when re-classifying, to bring their systems more and more nearly into line with the Council of Europe classification. Mr. R. Woodley (observer, International Union) suggested that the Commonwealth countries should consider adhering to the European Convention, rather than merely adopting its classification system.

After some discussion, Dr. Miles (New Zealand) put forward a proposal in the following terms: "The Conference recommends that Commonwealth countries who are considering a classification or secondary classification, adopt the International Classification, and to that end that those Commonwealth countries who have not already done so adhere to the European Convention on Patent Classification as early as possible". The Conference carried the resolution by a majority of 6 to 2, India and Pakistan voting against the resolution.

While voting against the above resolution, Mr. S. M. Ahmed (Controller of Patents and Designs, Pakistan) said that there was no objection to using the International Classification, as it might prove more useful. But he could not support the second limb of the resolution because (i) Pakistan was not a member of the International Union, (ii) adherence to the Union involved financial commitments and (iii) amendment of the patent law in Pakistan would be necessary. Earlier, his amendment to treat Dr. Miles's motion as two separate motions had been lost.

Convention on Patent Formalities and Reduction of Repetitive Work

The Conference considered the common measures which might be adopted (a) to facilitate the task of an applicant from one Commonwealth country seeking to protect his invention in other Commonwealth countries and (b) to reduce repetitive work in the various Commonwealth Patent Offices and thus lessen administrative costs.

Two resolutions, one moved by Dr. Miles (New Zealand) and the other by Mr. Ahmed (Pakistan), were adopted. Dr. Miles's resolution recommended those Commonwealth countries that are members of the International Union for the Protection of Industrial Property to adhere to the European convention relating to the formalities required for patent applications. Mr. Ahmed's resolution recommended exchange of information on the formalities in Commonwealth countries with a view to formulation of a convention particularly appropriate to the needs of those countries.

Financial Policies

The Conference then reviewed the basic financial policies of Commonwealth patent offices in relation to applicants, patentees, etc. Mr. Davies (Australia) explained the Australian deletions' viewpoint on the question of fee policy. Essentially this was that the grant and upkeep of the patent was a charge to be met by a fee covering the cost of services rendered, without producing surplus revenue.

Mr. Girling (United Kingdom) said that the Treasury's view was that the amount of fees taken in respect of patents, trade marks and designs should be sufficient to run those parts of the office that dealt with patent grants and trade marks and designs registrations. The Patent Office library and the Industrial Property Department were run at the cost of the public since they are more like other departments of the Board of Trade that do not charge fees.

Mr. V. G. Chowles (Registrar of Patents, Designs, Trade Marks and Copyright, South Africa) said that the income of his office was about £35,000 annually, while he assessed the cost of the office's services at about £5,000. Mr. Girling said that this was somewhat similar to the pre-war British position.

Dr. Miles (New Zealand) said that the position in the New Zealand office was much the same as South Africa, until 15 years ago. Recently the Patent Office was reorganised to provide better service to the public, and offer greater inducements to technical staff. Higher costs were met by increased fees, the policy being to develop the office and generally provide a more efficient system.

Mr. J.W.T. Michel (Commissioner of Patents, Canada) pointed out that this matter was now before the Royal Commission on the patent system in Canada. He said that it seemed to him

that the patent office should be self-sustained. However, fees must be kept in line with what inventors could pay, and it was undesirable to discourage overseas applications.

Dr. S. Venkateswaran (Registrar of Trade Marks, India) said that Indian Patent Office operated at a slight profit. The Patent Inquiry Committee had recommended that the Patent Office should not be regarded as a revenue-producing source; any profit should be put back into increased service to the public.

Mr. Wilmot (Australia) said that the matter largely turned on the services that the patent office gives to the community, some of which cannot be assessed financially. The Australian delegation considered that the applicant or patentee should be provided with all the services that they might reasonably require.

Mr. M. W. Triggs (observer, Chartered Institute and the British group of the International Association) said that this item was fundamental to the work of the Conference. On the official side, he said, any reduction in costs would be reflected in increased surpluses; but what of the patentee? He expressed the hope that the feeling would prevail that the patent system was "a kind of public service towards which the applicants should not be required to pay more than a reasonable proportion of the cost;" any reduction of costs should, he thought, be passed on to the inventor. Mr. Girling (United Kingdom) said that he had some personal sympathy with the opinion of Mr. Triggs. When the British rules were amended, an endeavour was made to keep down application fees, and make the cost of prosecutions low. After the grant, the fees became heavier, and later renewal fees had been considerably increased. The reason behind this development was that if the patent were paying the patentee he could afford to pay the renewal fee. If the patent were not remunerative the patentee could let it go, and to that extent clear the Register.

Mr. Robertson (observer, Department of National Development) referred to an earlier motion of Mr. Ahmed about publicity. This question, he said, was linked with the financial issue. His Department's interest, he pointed out, was in the vast amount of technical information held by patent offices, and readily accessible to industry. It seemed to him that the patent offices possessed an admirable amount of classified and codified material, and that industry was not sufficiently aware of its existence. He thought that the Conference provided an excellent opportunity for the heads of patent offices to take steps to ensure that industrialists knew of the material and had access to it. The usefulness of this would not be limited to under-developed countries.

Exchange of Information

The Conference proceeded to the consideration of the development of arrangements for mutual consultation and exchange of information on patent matters between Commonwealth countries. Mr. Ahmed (Pakistan) moved a resolution recommending mutual exchange of their publications between Commonwealth patent offices. The resolution was carried unanimously.

Another resolution of Mr. Ahmed recommending in principle visits, study tours and exchange of officers between the Commonwealth countries was also carried unanimously. Mr. Girling said that United Kingdom always welcomed officers from Commonwealth and other countries; he would not, however, wish to limit the practice to the sending of personnel by lesser offices to more advanced offices. He thought that much good could come from exchanges between all countries, though the staff position made this impossible for the United Kingdom at that time.

Agenda of Lisbon Conference

The Conference then proceeded to the consideration of matters expected to appear on the agenda of the Lisbon Conference of the International Union for the Protection of Industrial Property. Mr. Woodley (observer, International Union), introducing the item, gave a brief account of the aims and objects of the Paris Union and the restricted unions, and referred to the Bureau's intention to develop the English-speaking side of the Union.

Mr. Girling (United Kingdom) suggested that Conference might discuss the advisability of recommending to all Commonwealth countries who are not members of the Industrial Property Union that they should consider joining it. Mr. Ahmed (Pakistan) enquired whether there was any substantial industrial advantage, from the practical point of view, to small countries like South Africa and New Zealand from having joined the International Union. Mr. Girling pointed out that the existence of a number of bilateral agreements in this field was highly unsatisfactory; it was in the interest of good order for all Commonwealth countries to adhere to the main Paris Convention on Industrial Property. Dr. Miles (New Zealand) supported Mr. Girling, and

referred to the great commercial and practical advantages to be derived from the priority right conferred by the Convention.

Mr. Ahmed said that Pakistan, of course, was not a member of the Union. There was a definite advantage in the priority date, but since 95% of patent applications in Pakistan came from abroad, the main advantage would be to the overseas applicants. Mr. Chowles (South Africa) said that acquisition of priority rights was probably the only direct advantage from joining the Convention. There was, however, also the feeling of acting in unity with other countries.

Mr. Girling then moved, and Mr. Davies seconded the following resolution: "This Conference recommends to those countries of the Commonwealth who are not members of the Industrial Property Union that they should adhere to that Union."

Mr. Ahmed (Pakistan) said that the resolution did not appear to be within the terms of the agenda. He said that any observation that he had made should not be taken as suggesting that Pakistan was inherently against joining the Convention. The matter was one of high-level policy for government decision, and he could only suggest bringing the Conference's views to the notice of his government. Mr. Girling said that he was not committed to the resolution but thought that it might strengthen the hands of, say, the Indian delegate, if it were carried. Dr. Venkateswaran said that the resolution was directed towards India and Pakistan, and so far as India was concerned he would undertake to pass on the Conference's view to his government; he doubted, therefore, whether the resolution was necessary.

Mr. Wilmot (Chairman) ruled that the resolution was out of order, and directed, at the instance of Mr. Ahmed (Pakistan), that there should be included in the records of the Conference the following expression of opinion: "that those countries of the Commonwealth that are not members of the Industrial Property Union should adhere to that Union."

The Conference then proceeded to a detailed consideration of a paper submitted by Mr. Woodley (observer, International Union) under this item.

Miscellaneous Items

The Conference then considered a number of miscellaneous items not directly provided for in the agenda.

Mr. Ahmed (Pakistan) proposed that the Conference should endeavour to assess in terms of units of currency the value of the patent system. He pointed out that any consideration of the real value of the patent system was handicapped by the absence of facts and figures. The general feeling of the Conference was that while such an investigation, if practicable, would be of value, it was outside the scope of the present Conference.

Mr. Wilmot (Chairman) then introduced Mr. White (Commonwealth Librarian) who explained briefly the archival function of the National Library, with particular reference to patent specifications.

Dr. Miles (New Zealand) explained briefly research carried out by the New Zealand office into the problem of protection of artistic designs used in industry, and commented that the designs law seemed ineffective in this respect. If the work were an artistic work, he said, its proper place was under the law of copyright. He offered the results of the New Zealand investigation to other Commonwealth offices. Mr. Wilmot suggested that designs problems might also be made the subject of exchange of information between Commonwealth offices, and this was agreed to by the Conference.

PATENT NEWS

Patents of the Pakistan Council of Scientific and Industrial Research

Abridgements

A petrol gas plant. A. H. Chotani and S.M. Ishaq Ali (Pakistan patent 107505, May 29, 1957). The gas plant comprises a gas accumulator, a high speed blower, a device for bubbling air through petrol contained in a tank, and means for leading the mixutre of atomized petrol and air generated in the tank to the gas accumulator. The device for bubbling air through petrol is preferably made of a perforated hollow chamber kept submerged in the petrol.

Manufacture of light weight concrete. M. M. QURASHI, A. H. CHOTANI, A. K. M. AHSAN-ULLAH AND M.A. CHOUDHARI (Pakistan patent 107520, April 17, 1957).—The concrete is made by combining cement with rice husk ash preferably in a proporation of 1:1 by volume.

A process for the simultaneous production of refined shark liver oil and vitamin A concentrates alongwith the recovery of other therapeutically active by-products. S. MAHDIHASSAN, M. MOINUDDIN, S. MAQSOOD ALI AND S. ABDUL HAQ. (Pakistan patent 107859, February 28, 1957; Indian patent 60156, April 9, 1957).—The process comprises the steps of separating and filtering off stearine from the crude liver oil, refining the filtered oil to obtain refined oil containing vitamin A, saponifying the separated stearine fraction, extracting the unsaponifiable matter with ether, and separating the cholesterol present therein to yield vitamin A concentrate. The separation of stearine from crude liver oil is effected by storing the oil at about 15°C. The filtered oil is alkali-refined and deodorised by heating the oil with steam at a temperature not exceeding 115°C. The refined oil is standardised to any desired potency by blending it with cottonseed oil or any other oily diluent. The acid components of the saponified stearine may be converted into calcium salts.

A process for the continuous refining of sulphur ore. IQBAL AHMAD AND KARIMULLAH (Pakistan patent 108018, September, 19 1956).—Ground ore and a metallic salt solution heated to about 110°—160°C. are mixed in a vessel, and the mixture is transferred to a series of heated vessels at such a rate that by the time it reaches the end of the series the sulphur melts and forms globules. The hot mixture is poured into water and the solidified sulphur is separated from the gangue and diluted salt solution. A surface affective substance, e.g., kerosine oil or other products of petroleum distillation, is added towards the end of the series of heated vessels. A part of the diluted salt solution is recirculated in the separator and the rest is concentrated and reused in the process.

A process for the production of cottonseed oil based coating compositions. SALIMUZZAMAN SIDDIQUI AND M. ASLAM. (Indian patent 60100, April 3, 1957).— The process consists essentially in cooking cottonseed oil with rosin and metallic oxides until the resulting varnish acquires a desired viscosity depending on the quality of the varnish being produced. The metallic oxides which may be employed include calcium oxide, zinc oxide, lead monoxide and manganese dioxide. Cobalt acetate may also be added to enhance the quick-drying property of the coating compositions.

An improved wood preservative. SALIMUZZAMAN SIDDIQUI, M. ASLAM AND ASHHAD MEHDI. (Indian patent 60367, April 30, 1957).—The process for the production of the wood preservative comprises preparing copper soaps by causing a rosin oil fraction having an acid value of 70 to 95, obtained by destructive distillation of rosin and collected between 250°C. to 350°C., to react with copper sulphate dissolved in ammonia, and separating the copper soaps obtained by the reaction. The soaps may be dissolved in a solvent such as kerosine or mineral turpentine to obtain a solution of required strength.

A process for the production of an air entraining agent for cellular concrete. SALIMUZZAMAN SIDDIQUI, M. ASLAM AND JAMAL QUADIR. (Indian patent 60368, April 30, 1957).—The air entraining agent based on hydrolyzed protein solution is prepared by stabilizing the protein solution by the addition of ferrous ammonium sulphate and sodium sulphite. The protein solution may be prepared from hair, horns, hoofs, casein or blood.

Applications Filed

Improvements in or relating to a choola using firewood or cowdung cakes. LT. COL. MOHAMMAD ISHAQ AND C. KARAM ILAHI.—(Pakistan application 418/58, May 19, 1958).

Improvements in or relating to an angethi using charcoal or soft-coke. LT. COL. MOHAMMAD ISHAQ AND C. KARAM ILAHI.—(Pakistan application 419/58, May 19, 1958).

Improvements in or relating to a composition and a process for the production of waterproof sheets. SALIMUZZAMAN SIDDIQUI, M. ASLAM AND ASHHAD MEHDI.—(Pakistan application 761/58, September 8, 1958).

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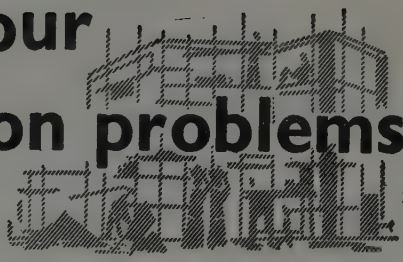

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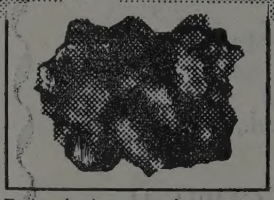

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